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NOTICE

There will be NO ISSUE of Section A - Physical Sciences Canadian Journal of Research in January or March 1946.

It is regretted that the number of suitable papers available is not sufficient to warrant publication in these two months.

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IDENTITY OF THE HYDROLYTIC BASE OBTAINED FROM *DELPHINIUM BROWNII* RYDB. WITH LYCOCTONINE[1]

BY LÉO MARION[2] AND R. H. F. MANSKE[3]

Abstract

The base obtained by hydrolysis of the chief alkaloid present in *Delphinium Brownii* Rydb. is shown to be identical with lycoctonine by comparison with an authentic sample of the latter. The perchlorate, picrate, and methiodide of lycoctonine from both sources have been compared and found to be identical.

Delphinium Brownii Rydb. has been shown to contain an alkaloid that on hydrolysis gives rise to methylsuccinic acid, anthranilic acid, and a crystalline base, the possible identity of which with lycoctonine was suggested (2). Lycoctonine was obtained by Schulze and Bierling (3) as a product of hydrolysis of the amorphous alkaloid lycaconitine isolated from *Aconitum lycoctonum.* More recently, Goodson (1) isolated from *Delphinium elatum* L. an alkaloid that on hydrolysis yielded methylsuccinic acid, anthranilic acid, and a base that he claimed was identical with lycoctonine, although he had no sample of authentic lycoctonine for comparison and failed to prepare any derivative from his base.

The hydrolytic base obtainable from *D. Brownii* has now been further studied and four of its salts have been prepared together with the methiodide. For purposes of comparison lycoctonine has been prepared by the hydrolysis of amorphous lycaconitine isolated from *Aconitum lycoctonum.* Lycoctonine together with its perchlorate, picrate, and methiodide are identical with the hydrolytic base obtained from *D. Brownii* and the corresponding salts and methiodide of this base. No depressions in melting points were observed upon admixture of the two bases or their corresponding salts. This result affords the first definite and unequivocal proof of the occurrence of lycoctonine in species of *Delphinium* and of *Aconitum.*

Since the empirical formula of lycoctonine has never been satisfactorily established, the hydrochloride and hydrobromide have been prepared besides the derivatives already mentioned. The analytical figures obtained from the base, its methiodide, and perchlorate are in best agreement with the formula $C_{20}H_{33}O_5N$. The analysis of the hydrochloride and the hydrobromide indicate

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that these two salts both crystallize with one mole of methanol. The picrate, however, is a salt of a complex nature that seems to involve two moles of the base per mole of picric acid. It has not been possible to arrive at any rational formula for the picrate. It is noteworthy that lycoctonine and all its derivatives are very difficult to analyse and the agreement between the analytical figures obtained and the calculated values in some cases is not too close. The formula $C_{20}H_{33}O_5N$, until substantiated by the characterization of simpler degradation products, is proposed only as that which fits best the numerous analytical data obtained from the base and its derivatives.

Experimental

Lycoctonine (from D. Brownii)

The hydrolytic base (2) was repeatedly recrystallized from aqueous methanol from which it separated as colourless, soft needles that sintered at 120° C. and melted at 139° C.* Found: C, 62.61; H, 8.84; N, 3.54; 3 OCH_3, 23.61%. Loss on heating *in vacuo* at the temperature of boiling toluene: 4.68%. Calc. for $C_{20}H_{33}O_5N \cdot H_2O$: C, 62.34; H, 9.09; N, 3.64; 3 OCH_3, 24.10; water of crystallization, 3.79%.

The perchlorate of the base was prepared in methanol with the aid of 65% perchloric acid and recrystallized twice from methanol–absolute-ether from which it was obtained as small, colourless prisms, m.p. 215° C. Found: C, 52.63; H, 7.59; N, 2.45; Cl, 7.14%. Calc. for $C_{20}H_{33}O_5N \cdot HClO_4$: C, 51.34; H, 7.27; N, 2.99; Cl, 7.59%.

When the base was treated with an acetonic solution of picric acid and the resulting solution diluted with absolute ether, the picrate crystallized in clusters of lemon-yellow needles. After recrystallization from acetone–ether, it melted at 154° C. Found: C, 53.99, 53.95; H, 6.73, 6.56; N, 6.11, 6.35%.

The hydrochloride was prepared from a solution of the base in methanol by the addition of a few drops of hydrochloric acid. When the resulting solution was evaporated to dryness under reduced pressure, it left a gummy residue, which was dissolved in a little dry methanol, and the solution diluted with ether just short of incipient turbidity. This solution, after standing in the cold for several days, deposited the hydrochloride as colourless, prismatic needles which, when recrystallized twice from methanol–ether, melted at 145° C. with effervescence, after shrinking at 104 to 105° C. Found: C, 57.48; H, 9.16; Cl, 7.20%. Calc. for $C_{20}H_{33}O_5N \cdot HCl \cdot CH_3OH$: C, 57.86; H, 8.72; Cl, 8.15%. Schulze and Bierling (3) report the melting point of lycoctonine hydrochloride as 75° C. (uncorr.). They do not mention having recrystallized the salt, which was undoubtedly impure.

The hydrobromide was prepared with hydrobromic acid by the same procedure used for the hydrochloride. It separated from methanol–ether as small, colourless prisms that shrank slightly at 225° C., turned black at about 260° C. and did not melt even at 360° C. Again, this is not in agreement with Schulze and Bierling (3) who give m.p. 88 to 89° C. for lycoctonine hydrobromide. Found: Br, 16.36%. Calc. for $C_{20}H_{33}O_6N \cdot HBr \cdot CH_3OH$: Br, 16.67%.

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* *All melting points are corrected.*

Lycoctonine methiodide

The methiodide was prepared from the base (3 gm.) dissolved in methanol (25 cc.) containing an excess of methyl iodide by heating in a sealed tube at 100° C. for 1.5 hr. The contents of the tube was evaporated to a small volume and hot ethyl acetate (5 cc.) added. On cooling, the methiodide was deposited as glistening yellow needles which, when recrystallized twice from methanol–ethyl-acetate, melted at 187° C. with some sintering at 184° C. Wt., 4 gm. Found: C, 49.53; H, 7.36; N, 2.32%. Calc. for $C_{20}H_{33}O_6N \cdot CH_3I$: C, 49.51; H, 7.06; N, 2.75%.

Crude Lycaconitine

Aconitum lycoctonum L, grown in a local garden, was dried and ground (dry wt., 2700 gm.). It was extracted with methanol in Soxhlets, the solvent largely distilled, and the residual syrup diluted with water and made acid to Congo with aqueous oxalic acid. After heating 24 hr. on the steam-bath the mixture was cooled and kept in the refrigerator for several days. It was filtered rapidly and the treatment repeated with the insoluble cake. The combined aqueous filtrate was thoroughly extracted with ether, basified with ammonia, and exhaustively extracted with chloroform. The chloroform extract was distilled to dryness on the steam-bath and the residue redissolved in an aqueous solution of oxalic acid. The resulting solution was filtered through a layer of charcoal, extracted with several portions of ether, basified with ammonia, and again repeatedly extracted with ether. This last extract, when distilled on the steam-bath to remove the solvent, left a residue consisting of a dark gum that weighed 9 gm. Extraction of the aqueous solution with chloroform yielded a further 2.5 gm. of base.

Isolation of Lycoctonine

The alkaloid obtained from the ether extract (9 gm.) was dissolved in 95% ethanol (60 cc.) and *N*/1 sodium hydroxide (30 cc.) added to the warm solution, which was kept on the steam-bath until most of the ethanol had evaporated. A little water was then added and the solution allowed to stand at room temperature overnight. Next morning the lycoctonine had crystallized out in clusters of fine colourless needles accompanied, however, by some gummy material. Warm acetone dissolved the lycoctonine but not the gum. Dilution of the acetone solution with water caused the base to crystallize in soft, silky needles that sintered at 120° C. and melted at 139° C. The total weight of purified lycoctonine was 2 gm. In admixture with the hydrolytic base obtained from *D. Brownii* it sintered at 120° C. and melted at 139° C. Found: C, 62.71; H, 9.30; N, 3.45%.

Some of the lycoctonine was converted to the perchlorate exactly as already described. After two recrystallizations from methanol–ether the salt melted at 215° C. either alone or in admixture with the perchlorate of the *D. Brownii* hydrolytic base. Found: C, 52.28; H, 7.51%.

The picrate of lycoctonine (m.p. 152° C.; found: C, 53.98, 54.10; H, 6.72, 6.64%) and the methiodide (m.p. 188° C.; found: C, 50.27; H, 7.40%) were prepared and found to have the same properties and melting points as the corresponding derivatives obtained from the hydrolytic base isolated from *D. Brownii*. In each case admixture with the corresponding compound failed to depress the melting point.

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THE SOURCE OF ACIDITY OF FRESH MILK FROM JERSEY COWS[1]

BY ALLEN D. ROBINSON[2] AND HERBERT S. SAMSON[3]

Abstract

Thirty samples of Jersey milk were analysed for each of titratable acidity, free carbon dioxide, carbonates, citric acid and citrates, casein, lactalbumin and lactoglobulin, and inorganic phosphates. Partial correlation coefficients were calculated for titratable acidity with each of the other variables. The only significant one was that between titratable acidity and inorganic phosphates. Therefore it is concluded that inorganic phosphates are the primary cause of the acidity of fresh milk.

The titratable acidity of milk, expressed as percentage lactic acid, is a standard test in many laboratories. Very high values are attributed usually to souring. It is recognized, however, that fresh milk has an appreciable titratable acidity of its own and that wide variations in it do occur. Obviously, titratable acidity is due in part at least—in the case of fresh milk it must be due wholly—to some normal constituent or constituents whose varying percentages induce fluctuations in the acidity value.

Larger variations are encountered between the milks of individual cows than between those of herds or between the mixed milks of regions. Values for milks from individual cows have been found by Rice and Markley (24) to be as low as 0.086% and by Caulfield and Riddell (6) to be as high as 0.295%. Reported figures for herd averages agree with those of Golding, Mackintosh, and Mattick (14) who found the acidity of samples of mixed milk taken weekly over a three-year period from 10 Shorthorn cows to range from 0.14 to 0.18% with a yearly average of 0.16%. These differences may be due to any of several factors. Houston (16) lists them as health of the cow, feed, age, breed, stage of lactation, interval of milking, and even the quarter of the udder from which the milk is drawn. Indeed, composition and acidity may vary during the course of a single milking. The effect of stage of lactation on titratable acidity is especially marked. Colostrum has the highest value. This drops rapidly during the first eight weeks of lactation to a fairly constant level. A further noticeable drop is observed towards the end of the lactating period. Houston (16), and Caulfield and Riddell (6), and others have stressed the effect of this factor.

A suggestion that acidity is carried over into the milk from an acid in the animal's food appears to be definitely disproved. McNab (20) found that the acidity of the milk from silage-fed cows was no greater than that of milk from cows receiving no silage. Sommer and Hart (27) included sulphuric

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acid in the ration to the extent of 120 cc. of concentrated acid daily for six days without affecting the acidity of the milk. Duncombe (9) fed cattle lactic, butyric, and phosphoric acids without altering the acidity of their milk. Anderson, White, and Johnson (1) found that corn-gluten feeding does not affect the titratable acidity. McInerney (19) found no relation between the kind of feed and the percentage of acid in the milk.

It has been emphasized by several investigators that the titratable acidity of milk is not a measure of the actual amount of acidity or hydrogen ion concentration of the milk. It is rather a measure of the buffer capacity of some milk constituents and their ability to resist the effect of added alkali on the milk between its normal pH and that of the turning point of the indicator—usually phenolphthalein. Vandevelde (30) calls the degree of acidity obtained by such a volumetric titration an arbitrary figure, while Grimes and Lyons (15) point out that low acidity milks may grade from good to very bad as judged by other tests. Davis (7) states that since the magnitude of the titration is affected by the total solid content of the milk—that is, its richness—a high titratable acidity may indicate a rich milk. Indeed a milk with a low total solids content may be slightly soured and yet give a normal titratable acidity.

High total solids and a high ash content have been associated with high titratable acidity in fresh milk by McInerney (19). Roeder and Radoi (25) found such a relation only when the composition of the total solids remains the same. Of the various milk constituents that might be responsible for the effect, particular attention has been directed to carbon dioxide, citric acid, casein, and inorganic acid phosphates. It has been claimed for each of these that it contributes in a greater or lesser degree to the titratable acidity of milk. Rice and Markley (24), using the results of analyses of 13 samples together with data reported in the literature, formed the constituents into hypothetical combinations. They concluded that casein contributes about one-half of the total titratable acidity; citrates, carbon dioxide, and lactalbumin, a small portion; and phosphates, the balance. They also advance the hypothesis that a condition of equilibrium exists between the citric acid, phosphoric acid, casein, and the bases, therefore the acidity due to any one of these depends upon its relation to the others. Sommer (26) concludes that the acidity of fresh milk is due principally to the phosphates and proteins in milk and to a lesser extent to the carbon dioxide and citrates. Wiley (32) prepared the various buffers in concentrations approximately equal to those in which they appear in milk and studied their buffer effects over different pH ranges. He found that between pH 6.6 and 8.0 phosphates and citrates increase titration with sodium hydroxide, while casein increases it slightly and calcium decreases it. He emphasized "the interdependence of the buffers, phosphate, citrate, casein and calcium."

Carbon dioxide may contribute somewhat to the acidity of milk. Van Slyke and Baker (28) found that the amount of carbon dioxide in milk and its titratable acidity decreased together in a general way. McDowall and

McDowell (18) found a general but not regular correspondence between acidity and the carbon dioxide content of cream. Peter (23) found that the acidity of milk decreased with the time and temperature of heating. He attributed this in part to the loss of carbon dioxide from it and in part to changes induced in casein by heating.

Giza (13) attributes the buffer action of milk chiefly to casein. So do Bordas (3) and Bordas and Touplain (4) who tested separately milk serum, the coagulum containing the insoluble salts, casein plus insoluble salts, and pure casein. Whittier (31) emphasizes, too, the importance of casein because of the similarity between the buffer curve for casein and those for milk.

Buchanan and Peterson (5) found that the titration curves of milk and disodium phosphate solutions are quite similar and conclude that phosphates are at least among the most important buffers of milk. Van Slyke and Bosworth (29) attribute the acidity to acid phosphates. This is supported by another kind of evidence. Olson (22, pp. 30-31) found that the phosphorus content of milk is high at the beginning of lactation, drops to a normal level in about six weeks and decreases gradually until the end of the lactation period. Reference has already been made to titratable acidity following the same course. Jacobsen and Wallis (17, pp. 5-28) found a decrease in the phosphorus content of milk during the first six months of lactation, after which time it increased steadily. However, they found that the values for Jersey milk were higher than those for milk from other breeds. This is known to be true in the case of titratable acidity.

All of this suggests that casein and inorganic phosphates may be responsible for most of the titratable acidity of milk. Carbon dioxide, citric acid, and lactalbumin may contribute in small measure or not at all to this property. Normal variations in casein and phosphate content of milk would account for variations in titratable acidity.

Probably we should distinguish between those substances that are primarily responsible for the titratable acidity and those that happen to be present in the milk as free acids. That there are several different free acids present may be demonstrated by routine analysis. And since they are free acids they will react with added alkali. But some of them may owe their presence to the fact that they are end-products of buffer activity and not to their being the original acids of the milk. Thus an acid phosphate might be buffered by a carbonate to form a secondary phosphate and carbonic acid. The carbonic acid would be the free acid of such a system and would react with any alkali added to it. But the acid phosphate would be the substance primarily responsible for the acidity of the system.

Information on the primary cause of acidity in fresh milk might be obtained by studying the composition of a series of milks and determining the partial correlation coefficient for each of its constituents with titratable acidity. The analyses should take note of all the constituents that might contribute to acidity, namely, carbon dioxide, carbonates, citric acid, citrates, casein, lactalbumin, lactoglobulin, and phosphates. If any of these constituents should show a significant partial correlation coefficient with titratable acidity, then it might be expected to contribute to the acidity. If the coefficient for any constituent is too small to be significant then that constituent could hardly be the cause of the acidity. We are justified in considering salts like citrates and carbonates since, as we have pointed out above, they may have been formed in the buffering of the original acid. As a matter of fact, while we speak of the proteins as though they are present in milk in the free form they are present for the most part as protein salts.

Experimental

The milks selected for study were from individual purebred Jersey cows. These were chosen because they were known to have higher titratable acidities than normal. An acidity value as high as 0.20% had been noted for the herd. Individual cows had been found to give milks with acidities varying from 0.14 to 0.27%. No attempt was made to select milk from cows in any particular stage of lactation. Rather they were taken at random from the herd. Each sample consisted of a quart of milk taken from the mixed complete morning milking of the individual cow, capped to prevent loss of carbon dioxide, and kept at icebox temperature until analysed. The analyses for carbon dioxide and titratable acidity were made on the fresh milk within three hours of milking. Samples were then preserved by the addition of 1 cc. of 36% formaldehyde and held in the icebox for further analyses.

Titratable acidity was determined by titrating a 50 cc. sample of milk with *N*/10 sodium hydroxide solution, using 10 drops of 1% phenolphthalein in alcoholic solution as the indicator. These quantities are several times those commonly used and should reveal slight differences between the milks.

Free carbon dioxide was determined by an adaptation of the method indicated by Faulk (10, pp. 226-228) for the determination of carbon dioxide in inorganic substances. The method, in brief, consists of releasing the carbon dioxide from milk by boiling, passing the gases through drying agents, and collecting the carbon dioxide in a weighed caustic potash absorption bulb. Carbonates were determined in a somewhat similar way. To the sample from which carbon dioxide had been removed by boiling, lactic acid was added. The mixture was boiled again for 30 min. The carbon dioxide released by the action of the acid and the heat was collected in a weighed caustic potash absorption bulb. Carbon dioxide is reported in terms of volumes per cent. Carbonates are reported as carbon dioxide in the same units.

Citric acid and citrates were determined by Beau's (2) modification of the method proposed by Deniges (8). Casein was ascertained by the method of Moir (21). Lactalbumin and lactoglobulin were determined together using Moir's procedure. Inorganic phosphorus was determined by analysing the milk serum from which casein, lactalbumin, and lactoglobulin had been removed, using the method of Fiske and Subarrow (12) for the determination of phosphates in blood and urine. These analyses are reported in the terms commonly employed for each.

The results of all the analyses are recorded in Table I. These are for 30 different milk samples. Employing these data the average and standard deviation for each constituent were calculated. Correlation coefficients were obtained using as variables

TABLE I

Analyses of milk

Sample No.	Titratable acidity as lactic acid, %	Carbon dioxide, volume %	Carbonates as carbon dioxide, volume %	Citric acid and citrates as citric acid, cgm./litre	Casein, %	Lactalbumin and lacto-globulin, %	Inorganic phosphates as phosphorus, mgm./100 cc.
1	0.180	5.51	0.53	28.0	2.44	0.53	67.9
2	0.190	6.22	1.12	26.5	1.81	0.53	71.4
3	0.154	6.09	0.63	69.5	2.48	0.44	61.9
4	0.183	5.89	0.48	35.5	3.14	0.47	64.3
5	0.165	7.19	0.58	44.5	2.38	0.65	66.2
6	0.169	5.17	0.86	45.7	2.52	0.54	60.0
7	0.140	8.13	0.96	53.0	2.60	0.57	61.7
8	0.158	7.62	0.51	32.5	2.51	0.60	64.3
9	0.176	7.09	0.86	12.0	2.79	0.70	62.7
10	0.151	5.45	0.68	14.7	2.82	0.48	63.5
11	0.176	7.67	0.96	59.0	3.24	0.46	65.9
12	0.176	5.66	0.56	51.5	3.34	0.54	56.5
13	0.169	3.72	0.56	42.7	3.21	0.56	63.7
14	0.183	4.82	0.71	43.0	2.50	0.75	64.8
15	0.187	5.40	0.61	50.0	3.38	0.66	67.1
16	0.187	4.94	0.73	32.5	3.36	0.66	72.6
17	0.183	5.12	0.86	40.0	3.02	0.57	65.7
18	0.205	4.18	0.68	26.5	3.56	0.69	71.6
19	0.174	5.51	0.53	62.0	3.06	0.52	62.0
20	0.193	8.27	0.74	19.0	3.64	0.65	72.3
21	0.160	7.73	0.86	60.5	2.59	0.50	55.9
22	0.162	6.12	0.74	59.0	3.07	0.70	54.2
23	0.187	6.89	0.76	32.5	2.93	0.50	69.9
24	0.140	8.45	0.20	56.0	2.57	0.53	56.3
25	0.165	9.48	0.69	48.5	2.92	0.67	59.0
26	0.190	7.61	0.43	26.5	2.26	0.50	67.3
27	0.153	6.43	0.76	47.2	2.57	0.60	57.2
28	0.165	7.55	0.66	50.0	3.00	0.57	60.9
29	0.173	7.95	0.84	54.5	2.76	0.54	61.7
30	0.155	7.10	0.94	48.7	2.68	0.60	55.1

1. Titratable acidity.
2. Carbon dioxide.
3. Carbonates.
4. Citric acid and citrates.
5. Casein.
6. Lactalbumin and lactoglobulin.
7. Inorganic phosphates.

Partial correlation coefficients for titratable acidity with each of the other variables were calculated. The formulae of Fisher (11) were used throughout. The results of these statistical studies are recorded in Table II.

TABLE II

STATISTICAL STUDY OF MILK COMPOSITION

Constituent	Average	Standard deviation	Correlation coefficient with titratable acidity	Partial correlation coefficient with titratable acidity
Titratable acidity, as % lactic acid	0.1716	0.0157	—	—
Carbon dioxide, volume %	6.499	1.368	−.3799	−.2397
Carbonates, as carbon dioxide, volume %	0.701	0.186	.0856	.0999
Citric acid and citrates, as citric acid, cgm./litre	42.38	14.50	−.4675	−.0467
Casein, %	2.838	0.411	.3552	.2984
Lactalbumin and lactoglobulin, %	0.576	0.080	.2159	.1373
Inorganic phosphates, as phosphorus, mgm./100 cc.	63.45	5.17	.7376	.6213*

* *The value of P for this correlation coefficient is less than .01. That is, the odds are greater than 99 to 1 that the correlation is not fortuitous but represents a real relation between the variables.*

Discussion

As indicated in Table II the partial correlation coefficient of titratable acidity and inorganic phosphate is significant. The probability against its being a chance happening is more than 99 to 1. However, the partial correlation coefficients of acidity–carbon dioxide, acidity–carbonate, acidity–citric acid and citrates, acidity–casein, and acidity–lactalbumin and lactoglobulin are too low to be considered significant. The probability that each of these values is the result of random sampling is greater than .1.

The value of .6213 obtained as the partial correlation coefficient of titratable acidity and inorganic phosphate is quite high. Ordinarily 30 is not a large number of samples to analyse for purposes of statistical analysis. A high correlation is necessary to indicate a relation between the two variables. The probability of chance happening in this case is less than .01. The positive values indicate a direct relation. When individual values are plotted on graph paper the relation is shown to be linear. These findings show that the inorganic phosphates of the Jersey milks examined are responsible for their titratable acidities. The titratable acidity of fresh milk of other breeds may be caused by the same constituent.

It is not likely that the titratable acidity of fresh milk is due entirely to its phosphate content. Indeed the analyses reported here show varying percentages of other acid substances in milk. A part of these must exist as free acids which are neutralized in the titration of the milk. It has already been suggested that the presence of such constituents may be the result, not the cause, of acidity: that is, they are end-products of reactions between buffers and stronger acids. Furthermore, the results of other researches to which reference has been made confirm that an equilibrium of several buffer constituents does exist. However, the results of this experiment indicate that inorganic phosphates are the primary cause of the titratable acidity of fresh milk.

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THE EFFECT OF SOLVENT AND TEMPERATURE ON THE VISCOSITY OF THE POLYSACCHARIDE OF IRISH MOSS AND THE EFFECT OF SOLVENT ON ITS INITIAL GELATION[1]

By F. A. H. Rice[2]

Abstract

The viscosity of aqueous extracts of Irish moss (*Chondrus crispus*) has been found to depend mainly on the concentration of the neutral salts present in the solution. Samples of dialyzed polysaccharide, however, show considerable variation. The relation between the ***specific viscosity*** and the ***concentration*** in dilute aqueous solutions and formamide is such that $\eta_{sp} = ac_v + bc_v^2$, where η_{sp} is the ***specific viscosity***, c_v the ***concentration***, and both a and b are constants. In aqueous solution these constants are decreased by the addition of neutral salts. A rise in temperature causes a decrease in viscosity. This decrease is less rapid for solutions in formamide and aqueous solutions containing neutral salts. The effectiveness of individual salt solutions in promoting a decrease in viscosity coincides with their effect in producing precipitation of the polysaccharide. The order of decreasing effectiveness was: potassium chloride, calcium chloride, sodium chloride. When the concentration of gelose is such that gelation takes place on standing, measurements of viscosity become irregular and are not reproducible. The concentration of gelose at which the regular viscosity measurements are obtained decreases with increasing concentration of neutral salts. The rigidity of the gels so formed also decreases. The firmness of a gel seemingly depends on the concentration and type of neutral salt, as well as on the ***intrinsic viscosity*** of the polysaccharide. The intrinsic viscosity is defined as: the limit of the specific viscosity as the concentration approaches zero.

Introduction

It is well known that the viscosity of a solution of large molecules is dependent on the average particle size of the solute. This has been observed in such polymers as cellulose acetate, polyisobutylene, polyvinyl chloride, polystyrene, and natural rubber (1, 4, 5, 12, 14). The viscosity is also influenced by the solvent and the temperature at which the measurements are made. For example, the viscosity of a solution of rubber in benzene is decreased 40% by the addition of 15% methanol (6).

Various attempts have been made to show a relation between the viscosity and the average particle weight without any positive success. Recently, however, the theory of the solution of moderately dilute solutions of high polymers originated by Guth and Gold (7) and Simha (18) has been expanded by Huggins (9, 10, 11) with the result that the *specific viscosity*, η_{sp}, divided by the volume concentration c_v is known to be given by the equation: $\frac{\eta_{sp}}{c_v} = [\eta] + k'[\eta]c_v^2$, where $[\eta]$ is the limiting value of $\frac{\eta_{sp}}{c_v}$ for zero concentration and k' is a constant characteristic of the system. The *specific viscosity* is defined as: $\frac{\eta_c}{\eta_o} - 1$, where η_c is the viscosity of the solvent-solute system and

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η_o the viscosity of the solvent. More simply we may write the relation as $\eta_{sp} = ac_v + bc_v^2$. The same result has been obtained empirically by Schulz and Blaschke (17). In the formula: $\eta_{sp} = ac_v + bc_v^2$ the constants are found to be affected by both solvent and temperature (13). Theoretically $[\eta]$ should be independent of the solvent and related to the molecular weight, but this has been seldom realized in practice.

The polysaccharide of Irish moss, often referred to as gelose or carrageen, is highly viscous in aqueous dispersion and forms a stiff gel in a concentration of about $2\frac{1}{2}\%$ (8). Companies using Irish moss have found that the viscosity and the concentration at which a gel forms, as well as the resultant firmness of the gels at equal concentrations, differ widely with individual samples. This was confirmed on a large number of samples prepared by the author.

All samples of undialyzed gelose contain various amounts of the salts present in sea water, principally sodium chloride. In addition gelose can be salted out of solution (8), and it has been shown that alkali and alkaline earth salts will increase the firmness of the gels (15, 16). Accordingly it was thought that a study of the effect of several common, neutral salts on the viscosity and gel-forming properties of gelose might help to explain the observed variations in these physical properties, which are being used extensively in various commercial preparations in the food and pharmaceutical industries.

Experimental

The gelose used was prepared from samples of Irish moss collected and bleached in Prince Edward Island. The sample, after being washed for 12 hr. in cold running water, was extracted in distilled water for six hours on the boiling water-bath. The extract was filtered through Hyflo Super-Cel (Johns Manville) on a Büchner funnel, concentrated at 95 to 100° C., precipitated in four volumes of ethanol, and, after redissolving in distilled water, dialyzed for 48 hr. against frequent changes of distilled water. The solution was then concentrated *in vacuo* at 35 to 40° C., and again precipitated in 85 to 90% ethanol. The extract was dried by successive changes of absolute ethanol and anhydrous ether and kept in a vacuum desiccator over fused calcium chloride. The product, which was of a fibrous nature, was ground in a mortar to give a fine, snow-white powder.

Viscosities were measured by means of a Stormer viscosimeter. The weight used was such that the time measured by a stop watch reading to 0.1 sec. ranged between 30 to 40 sec. The solutions were maintained at a temperature of 30° ± 0.5° C. in a bath.

Neither the *intrinsic* nor the *specific viscosity* of different samples of gelose at any particular concentration was uniform when treatment in moistening agent, time of bleaching, and drying previous to extraction varied, although the conditions of extraction were the same. Fig. 1 shows the plot of *specific viscosity* versus the volume concentration for three representative samples. Samples 1, 2, and 3 were exposed to sunlight for increasing lengths of time.

The samples studied showed that at concentrations below about 7 gm. per litre, η_{sp} bore a linear relation to c_v. Above 7 gm. per litre the line became progressively curved in the direction of the *y*-axis.

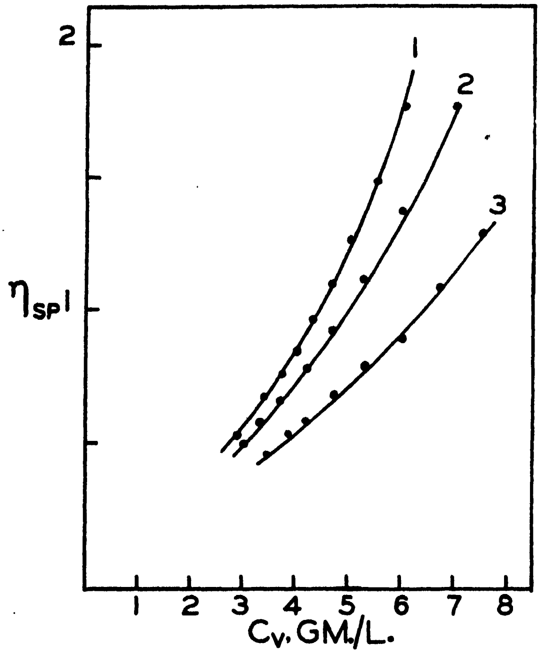

FIG. 1. *The relation of specific viscosity to concentration for three different extracts of gelose.*

To determine the effect of solvent on the viscosity of a gelose solution, samples were dissolved in the solvents indicated in Fig. 2 and their viscosities determined at a number of concentrations. It will be seen that in each case η_{sp}/c_v is linearly related to c_v. The constants *a* and *b*, of which *a* is the value obtained by extrapolation to zero concentration and *b* is the tangent of the angle made with the *x*-axis, are decreased in solvents other than distilled water. The solvent affects *b* to a greater extent than *a*. At equal concentrations potassium chloride is more effective than sodium chloride. The effect of calcium chloride is not shown but it was midway between the effects of potassium and sodium salts at equal concentrations. Formamide is intermediate in effect between 0.01% solutions of potassium and sodium chlorides.

The solvent also modified the decrease in viscosity due to increased temperature. Measurements made between 25° and 50° C. at concentrations of 1, 3, and 5 gm. per litre of gelose show a progressive loss in viscosity as the temperature increases that is more marked in distilled water than in either formamide or 0.03% sodium chloride solution. Table I shows the results obtained in a 1 gm. per litre solution of gelose. The viscosity at any temperature is decreased in the order: distilled water, formamide, 0.03% sodium chloride solution. The rate of decrease is reduced in the same order.

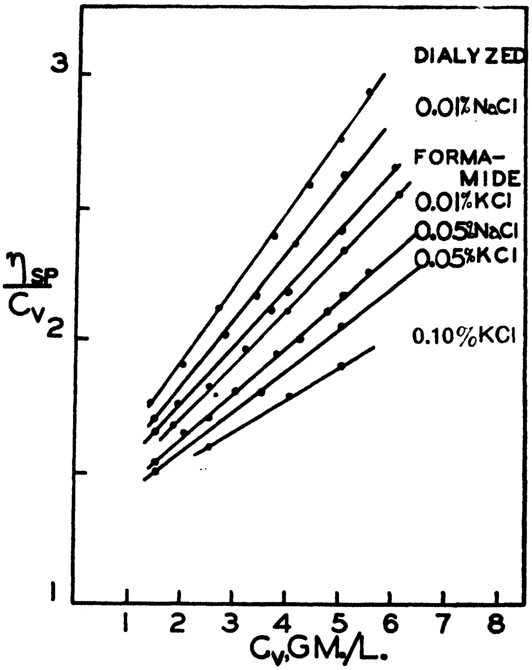

FIG. 2. *The effect of solvent on the viscosity of gelose solutions.*

TABLE I

EFFECT OF TEMPERATURE ON THE VISCOSITY OF GELOSE IN SEVERAL SOLVENTS

Temperature, ° C.	η_{sp} in:		
	Distilled water	Formamide	0.03% NaCl
25	5.78	5.50	4.25
30	4.89	4.51	3.55
35	3.99	3.60	2.95
40	3.05	2.82	2.21
45	2.10	1.99	1.53
50	1.38	1.12	0.96

When the concentration of a gelose solution was increased to a point where gelation would occur on standing (usually about 20 gm. per litre) measurement of viscosity became irregular and could not be reproduced. If neutral salts were added to a gelose solution too dilute to form a gel ordinarily, the viscosity was lowered and a critical concentration of salt could be reached at which the measurement of viscosity became irregular and if left for a time the solution would gel. These gels were very weak and formed only above a concentration of about 5 gm. per litre of gelose. Below this concentration of gelose the polysaccharide was precipitated from solution as a gelatinous precipitate.

Fig. 3 shows the effect of adding 0.06 and 0.25% of potassium chloride to an extract that would ordinarily gel at 19 gm. per litre. It will be seen that gelation was induced at the lower concentration of 7.5 and 6.5 gm. per litre, respectively, by the addition of the salt. The same effect was observed with sodium and calcium chlorides to a lesser degree. The gels formed at these low concentrations were very weak and apparently their firmness depended on the concentration of gelose.

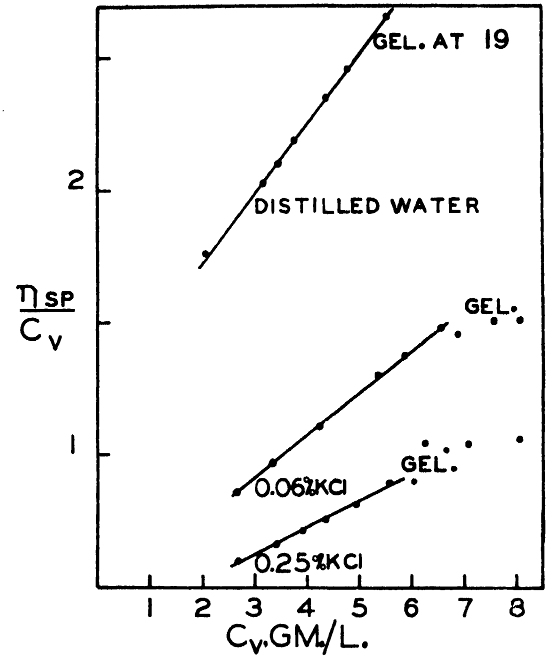

Fig. 3. *The effect of increasing concentrations of potassium chloride on the initial gelation of a gelose solution.*

The *intrinsic viscosity* of the gelose solution also affected the point at which initial gelation occurred. Three samples (Fig. 4) showing different viscosities were treated at a concentration of 6 gm. per litre with sufficient potassium chloride to form a 0.1% solution. It will be seen that the gels first formed at approximately 6, 7, and 8 gm. per litre, the more viscous solutions showing an earlier formation of the gel induced by the same concentration of potassium chloride. If the concentration of the gelose in solution was increased to about 20 gm. per litre in each case, the firmness of the gels was easily seen without measurement to be parallel to the original viscosities of the solutions.

Table II shows the approximate concentration necessary to precipitate the gelose from solutions containing 5 and 2.5 gm. per litre, using potassium, sodium, and calcium chlorides.

Fifty-milligram quantities of the indicated salts were added to 10 ml. of the gelose solution until precipitation took place. The salt concentration was calculated from the amount added.

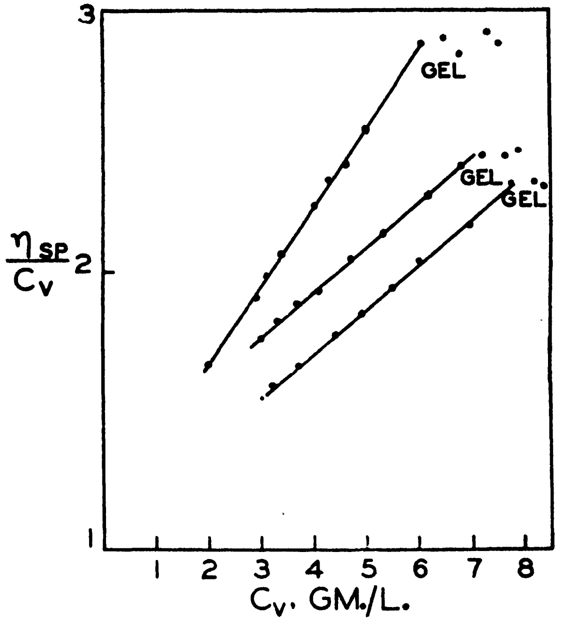

FIG. 4. *The effect of a concentration of 0.1% of potassium chloride on the initial gelation of three gelose solutions of different viscosities.*

TABLE II

CONCENTRATION OF NEUTRAL SALTS REQUIRED TO PRECIPITATE GELOSE FROM SOLUTION

Conc. gelose, gm. per litre	Conc. of salt required to precipitate gelose, %		
	KCl	NaCl	$CaCl_2$
5.0	0.39	1.86	0.42
2.5	0.46	1.84	0.34

It will be seen that the effectivness of the several salts in precipitating the gelose is in the same order as their effect in decreasing the viscosity of the solution.

Discussion

The polysaccharide of Irish moss in dilute solution shows a relation between the viscosity and the concentration that is represented by the equation $\eta_{sp} = ac_v + bc_v^2$. The values of the constants are undoubtedly determined by the average size and shape of the macromolecules and are affected by the solvent in which the viscosity is determined.

Alfrey, Bartovics, and Mark have demonstrated that the viscosity of a polymer is steadily decreased in increasingly poor solvents or solvent–non-solvent mixtures (2). They have also shown that increased temperature modifies and can in some cases increase the observed viscosity. This is explained in the case of linear polymers as due to the curling of the macromolecule, the degree of which depends on the solubility of the polymer in the medium. In any case, the observed effect is a decrease in the value of the constant *b* and a lesser decrease for *a* in the progressively poor solvents.

Huggins (13), using data from the literature on polystyrene and polybutene solutions, has shown that the η_{sp}/c_v values for solutions of a given polymer in different solvents is a function of the proportions of the poor solvent that are required to produce precipitation of the solid phase.

It must be admitted that work of this nature has been done using non-aqueous solvents and not salt solutions, but it is of interest that essentially the same results are obtained with an aqueous solution of gelose if we consider the effect of the added neutral salts to be one of decreasing the solubility of the polysaccharide. That the viscosity of gelose is decreased in formamide, in which it was found to be difficult to dissolve to the extent of 8 gm. per litre, agrees with this hypothesis.

If we consider gelation to occur as a consequence of the precipitation and arrangement of long molecules in a solution, the noted effect of neutral salts in causing earlier gelation is to be expected. The magnitude of the effects of individual salts might be related to their modifying the solubility of the gelose. This would correspond to the observed solubility of the gelose in salt solutions. On the other hand, one would expect that the firmness of the gel would be dependent not only on the precipitation and arrangement of the particulates, which would occur on initial gelation, but on the size and type of the macromolecules or particulates themselves. Bartovics and Mark (3) consider that k' might be a measure of the stiffness of the polymer chain. Alfrey, Bartovics, and Mark also suggest that in a mixture of macromolecules that have different chain lengths and different internal architecture (e.g., branching), precipitation takes place according to the $[\eta]$ values rather than the molecular weights (2).

It must also be remembered, however, that gelose contains ionized calcium (8), which undoubtedly would affect the viscosity in salt solutions inasmuch as added salts, such as potassium chloride, would give rise to an equilibrium between the calcium of the gelose and the added metal. This would mean that a salt solution would contain a mixture of the salts of gelose, the properties of which would depend on the individual properties of the components.

Acknowledgments

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A METHOD OF MEASURING THE STABILIZING POWER OF EXTRACTS OF IRISH MOSS[1]

By F. A. H. Rice[2]

Abstract

A method of measuring the stabilizing power of extracts of Irish moss has been developed. This is based on the quantity of calcium oxalate, expressed as grams per gram of dry extract, held in suspension under specific conditions. The logarithm of this quantity plotted against the concentration of gelose gave a straight line relation. Results were accurate within 1%. Condition of measurement required a temperature below 60° C., pH between 5.5 and 8.5, and a low concentration of neutral salts. Results were compared with those obtained with chocolate powder stabilized in milk. An equation $M = K/t^p c^n$ has been developed and verified, in which the constant K is shown to be numerically an index of stabilizing power, and where M is the number of grams of calcium oxalate held in suspension per gram of extract at a concentration of c grams of extract per 100 ml. after centrifuging for time t. K, p, and n are constants: p and n represent the tangents of lines plotted for the logarithms of M against t and c, respectively.

Introduction

Aqueous extracts of Irish moss (*Chondrus crispus*) have recently been used extensively as a stabilizing agent to hold insoluble material in suspension. The largest use occurs in the stabilization of chocolate milk. Thus approximately 0.03% of dried, purified extract in 500 ml. of milk will prevent the sedimentation of 37 gm. of chocolate. The exact concentration required to hold a given amount of chocolate varies considerably with each sample of extract, and some samples, although forming viscous solutions and firm gels, do not possess this property. The degree to which a sample will prevent sedimentation is sometimes known as the "stabilizing power" of the sample. In the case of chocolate in milk it is usually given as the number of milligrams of dried extract required to maintain in suspension a definite quantity of chocolate in a given quantity of milk.

The active agent and main chemical substance present in these extracts is a polysaccharide sulphate sometimes called "gelose" or "carrageen," (1, 4, 6). Insoluble inorganic salts such as silver chloride, barium sulphate, and calcium oxalate could not be removed completely from a gelose solution, particularly when they had been freshly precipitated in that solution. It was considered that the amount of these salts held in suspension might serve as a measure of the stabilizing power of the extract.

Before attempting to show a definite relation between the amount of an insoluble salt held in suspension and the stabilizing power as measured in other ways, it was necessary to investigate the limiting factors that might affect the rate of sedimentation of the suspended material in a gelose solution.

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Contribution from the Fisheries Research Board of Canada and the Department of Biochemistry, Dalhousie University, Halifax, N.S.

[2] *Demonstrator in Biochemistry, and Temporary Scientific Assistant, Fisheries Research Board.*

Precipitations of silver chloride, barium sulphate, barium oxalate, and calcium oxalate were tried initially. Attempts to filter and weigh the excess barium sulphate and silver chloride proved very difficult. The formation of an oxalate and the estimation of the sediment by titration against potassium permanganate proved relatively simple.

Method

Quantities of a 0.50% gelose solution were pipetted into 15 ml. graduated centrifuge tubes to give the required concentration or series of concentrations between 0.01 and 0.10 gm. per 100 ml. The contents of each tube was then diluted to 8 ml. with distilled water. To ensure complete solution it was warmed at 60° C. and gently agitated. On cooling, 1 ml. of 0.10 M calcium chloride solution was added and, after mixing, 1 ml. of 0.10 M sodium oxalate solution was run in drop by drop, the tubes being tapped gently to ensure an even distribution of the precipitate. They were allowed to stand 5 to 10 min. and then centrifuged at 2800 r.p.m. for a known length of time. After the supernatent liquid was poured off, the precipitate was washed twice with 0.2% ammonia solution, centrifuging for about five minutes after each washing. The tubes were then drained on filter paper and 3 ml. of 5% sulphuric acid was added. The calcium oxalate was then titrated against $N/50$ potassium permanganate (2). The amount of calcium oxalate held in suspension was obtained by subtracting this figure from a blank containing no gelose. This figure agreed with that calculated from the amounts of calcium chloride and sodium oxalate used.

Experimental

To ascertain the degree of precision of the method four tubes containing 0.5% gelose and four tubes containing 0.02% gelose, to all of which had been added equivalent amounts of calcium chloride and sodium oxalate, were centrifuged for 5 and 20 min. each. It will be seen from Table I that the results are reproducible within about 1%.

TABLE I

Reproducibility of results

Tube No.	Mgm. per ml. of oxalate suspended			
	After centrifuging 5 min.		After centrifuging 20 min.	
	0.05% gelose	0.02% gelose	0.05% gelose	0.02% gelose
1	6.72	4.67	2.86	2.62
2	6.66	4.64	2.87	2.62
3	6.72	4.61	2.88	2.63
4	6.66	4.67	2.87	2.61

Violent stirring or shaking immediately after the formation of the precipitate of calcium oxalate caused a decrease of more than 10% in the amount suspended. This was also true when the tubes were centrifuged immediately. After standing 15 min. results were relatively constant as shown in Table II.

TABLE II

EFFECT OF STANDING AFTER THE ADDITION OF SODIUM OXALATE

Time, min.	Mgm. per ml. of oxalate suspended	
	0.05% gelose	0.02% gelose
0	4.35	3.64
5	3.76	3.22
10	3.75	3.21
15	3.76	3.22
30	3.75	3.22
600	3.76	3.21

The addition of an excess of calcium chloride and sodium oxalate caused an increased sedimentation which, at a concentration of 0.05% gelose, became measurable when more than 2 ml. of each reagent were used. This increased sedimentation was associated with a partial precipitation of the gelose from solution. When less than 0.25 ml. of each reagent was used there was no measurable sedimentation after centrifuging 10 min.

Changes in temperature up to 60° C. had no measurable effect (Table III). After the addition of the calcium chloride, the tubes were heated for five minutes at the indicated temperature, and the sodium oxalate was added. After another five minutes they were centrifuged for 15 min. and the determination of calcium oxalate was made as before. Above 60° C. irregular results were obtained.

TABLE III

EFFECT OF TEMPERATURE

Conc. of gelose, %	Mgm. per ml. of oxalate suspended		
	22° C.	56° C.	90° C.
0.10	6.60	6.71	6.56
0.06	5.10	5.08	5.13
0.04	4.04	4.06	3.98
0.02	3.08	3.10	3.06

Sodium chloride, potassium chloride, and calcium chloride, when added in excess, increased sedimentation. Various amounts of each salt were added before the addition of the sodium oxalate and the tubes centrifuged for 10 min. The increased sedimentation varied with the amount and the nature of the salt used (Table IV).

TABLE IV

EFFECT OF NEUTRAL SALTS

Conc. of gelose, %	Additional conc. of salt, moles	Mgm. per ml. of oxalate suspended with added		
		NaCl	KCl	$CaCl_2$
0.05	0.05	3.74	3.75	3.77
	0.1	3.74	3.74	3.75
	0.2	3.73	2.26	2.68
	0.3	3.72	2.05	1.98
	0.4	3.72	—	1.28
0.01	0.05	1.60	1.61	1.62
	0.1	1.61	1.60	1.60
	0.2	1.60	1.22	1.34
	0.3	1.21	—	—
	0.4	0.83	—	—

A change in pH between 5.5 and 8.5 had little effect. Above and below this, however, the calcium oxalate held in suspension was decreased. Results are shown in Table V. The pH was adjusted with sodium hydroxide and acetic acid and measured by means of the glass electrode. The concentration of gelose was 0.05% and the time of centrifugation was 11 min.

TABLE V

EFFECT OF pH

pH of solution	3.1	3.8	5.0	5.5	6.5	7.0	8.5	10.4	11.6
Mgm. per ml. of oxalate suspended	1.92	2.43	2.50	3.71	3.74	3.74	3.78	2.45	1.92

By way of comparison, equivalent amounts of barium hydroxide and oxalic acid were used to form barium oxalate under identical conditions as for calcium oxalate. The results were parallel to those obtained with calcium oxalate (Table VI). It should be noted that in this case no sodium chloride was formed by the reaction between the reagents.

TABLE VI

COMPARISON OF BARIUM AND CALCIUM AS OXALATES

Conc. of gelose, %	Barium, mgm. per ml.	Calcium, mgm. per ml.	Ratio barium : calcium
0.10	2.75	3.06	0.89
0.08	2.71	3.01	0.90
0.06	2.58	2.87	0.89
0.04	2.50	2.77	0.90

The amount of calcium oxalate held in suspension at various concentrations of gelose and after various times of centrifugation was determined. Concentrations from 0.01 to 0.1% gelose were used and at each concentration a series was centrifuged from 10 to 45 min. The number of grams of calcium oxalate retained in suspension per gram of gelose after any particular time of centrifugation was found to be logarithmically related to the concentration of gelose (Fig. 1). The same logarithmic relation was observed at any given concentration when the time of centrifugation was varied (Fig. 2).

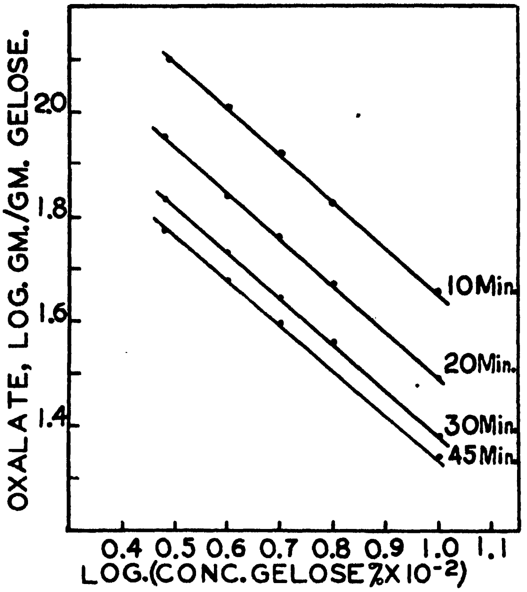

FIG. 1. *Influence of concentration of gelose on oxalate held in suspension.*

A number of samples were tested for this relation and it was found to be true in each case. The tangent of the lines relating the amount of calcium oxalate to the concentration of gelose or time of centrifugation, however, was found to vary with the individual sample. The extrapolated value for zero concentration and zero time of centrifugation also varied with the sample.

Because of this logarithmic relation we may write for any given sample: $M = K/t^p c^n$, where M is the number of grams of calcium oxalate held in suspension per gram of gelose at a concentration c grams of gelose per 100 ml. after centrifuging for time t. K, p, and n are constants: p and n represent the tangents of lines plotted for the logarithms of M against t and c, respectively. K can be obtained by substitution at any concentration where the calcium oxalate in suspension is known.

To check the calculated with the observed values these constants were determined on a sample of gelose. Values were calculated for various concentrations and times of centrifugation and actual measurements made. The results agreed within less than 1% (Table VII).

TABLE VII

AGREEMENT IN OBSERVED AND CALCULATED VALUES

Time of centrifugation, min.	Conc. of gelose, %	Grams oxalate per gram gelose	
		Calculated	Observed
20	0.03	893	892
20	0.05	575	576
10	0.03	1190	1210
15	0.05	671	670
35	0.05	421	428
10	0.10	457	452

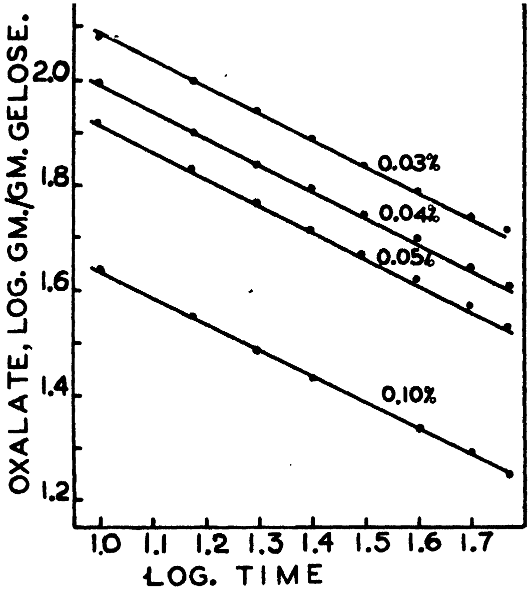

FIG. 2. *Influence of period of centrifugation on suspension of oxalate in gelose.*

A series was directly compared to determine whether a relation existed between the constants obtained with calcium oxalate and the stabilizing power of the gelose towards chocolate in milk. To measure the stabilizing power of different samples of gelose as regards chocolate, 36.6 gm. of chocolate was added to each of a series of bottles containing 0.02 to 0.06% of gelose at intervals of 0.005% in 500 ml. of milk. The milk tested 2% butter fat. The lowest concentration of gelose that retained the chocolate in suspension after 48 hr. was taken as the index of stabilizing power. If the number of grams of chocolate held in suspension per gram of gelose is calculated from the concentration of gelose necessary to stabilize the chocolate, as is done in the case of the calcium oxalate, it is found (Table VIII) that the amount of chocolate is directly related to the constant K within the unavoidable 10% error made in the determination of stabilizing power by means of chocolate.

TABLE VIII

COMPARISON OF CONSTANTS OBTAINED FROM CALCIUM OXALATE APPLIED TO CHOCOLATE IN MILK

Sample No.	K	p	n	Chocolate held in suspension per gram gelose	K/chocolate per gram gelose
2	211	0.525	0.860	162.8	1.38
3	202	0.254	0.748	146.4	1.30
4	7.3	0.217	0.140	<24.4	—
5	4.1	0.790	0.326	<24.4	—
6	247	0.101	0.467	183.0	1.35
7	329	0.428	0.325	244.0	1.35
8	177	0.152	0.620	106.7	1.60
9	215	0.314	0.208	—	—

In the simplest form of the proposed method, constants can be determined by measuring the calcium oxalate retained in suspension at two concentrations of gelose after two different periods of centrifugation at each concentration. Suppose, for example, m_1, m_2 grams of oxalate per gram of gelose are suspended at concentrations c_1, c_2, respectively, after centrifuging t_1 minutes, and m_3, m_4 at the same concentrations after centrifuging a longer time t_2. Then:

$$n = \frac{\log m_2 - \log m_1}{\log c_2 - \log c_1} \text{ or } \frac{\log m_4 - \log m_3}{\log c_2 - \log c_1}$$

$$p = \frac{\log m_1 - \log m_3}{\log t_2 - \log t_1} \text{ or } \frac{\log m_2 - \log m_4}{\log t_2 - \log t_1}$$

At concentration c_1 or c_2, K can be determined from the equation $K = m\,c^n t^p$.

Discussion

From the evidence presented it would seem that the amount of calcium oxalate held in suspension in a gelose solution at various concentrations and after various times of centrifugation can serve to determine several constants which vary with the gelose sample. The exact meaning of these constants is not clear. Ewe (3) has shown that methylene blue will precipitate gelose from solution. He suggested that the dye was adsorbed, forming an insoluble complex. It may be that the observed stabilizing power is an adsorption phenomenon associated with particulates of small diameter.

Adsorption has been found to follow a certain rule in regard to the quantity taken up by a given weight of adsorbent. This is usually stated as $a = Ac^{1/n}$ (the so-called Freundlich adsorption isotherm). If the logarithms of this equation are taken we get $\log a = \log A + 1/n \log c$. The two sides of this equation bear a linear relation to each other. The similarity between this and the effect noted for calcium oxalate in gelose solution is evident.

Mason and Weaver (5) showed that "all suspensions should sediment under the influence of gravity" and "this system should show a logarithmic gradient of concentration." We might assume that the suspended material would therefore be thrown out of suspension logarithmically under the influence of centrifugal force and hence the material in suspension would be logarithmically depleted.

It is believed that these suggestions might account for the observed relations of stabilization in gelose solutions.

Acknowledgments

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SYNTHESIS OF A NEW α-AMINO ACID, S-METHYL-β,β-DIMETHYLCYSTEINE[1]

By KENNETH SAVARD[2], EDWIN M. RICHARDSON[2], AND GORDON A. GRANT[3]

Abstract

A new sulphur-containing α-amino acid, S-methyl-β,β-dimethylcysteine has been prepared from S-benzyl-β,β-dimethylcysteine. These two compounds and the intermediate β,β-dimethylcysteine may be of physiological importance.

S-Benzyl-β,β-dimethylcysteine has been prepared by the addition of benzyl mercaptan to α-benzoylamino-β,β-dimethylacrylic acid, its azlactone, and methyl ester, followed by hydrolysis.

In addition to the above three new sulphur-containing α-amino acids, the following compounds are described, as far as the authors are aware, for the first time: methyl α-benzoylamino-β,β-dimethylacrylate, S-benzyl-N-benzoyl-β,β-dimethylcysteine and its methyl ester, the hydantoin of S-benzyl-β,β-dimethylcysteine, and S-benzyl-β,β-dimethylcysteine ethyl ester hydrochloride, and helianthate.

Introduction

The present study was undertaken in these laboratories to make available for physiological studies the hitherto unknown α-amino acid, S-methyl-β,β-dimethylcysteine. In the synthesis of thiol and thioether α-amino acids, du Vigneaud and co-workers have introduced a convenient approach by first synthesizing the benzylthiol derivative of the desired compound. The benzyl group is then easily removed by reduction in liquid ammonia to give the thiol amino acid (14), or it may be replaced by an alkyl group by reduction and subsequent treatment with the appropriate alkyl halide in liquid ammonia to give the alkylthiol amino acid (4, 5). Accordingly S-benzyl-β,β-dimethylcysteine was prepared by the addition of benzyl mercaptan in the presence of sodium methoxide to the azlactone of α-benzoylamino-β,β-dimethylacrylic acid, followed by hydrolysis. S-Methyl-β,β-dimethylcysteine was then obtained from S-benzyl-β,β-dimethylcysteine by reduction of the latter with sodium in liquid ammonia followed by treatment with methyl iodide.

A study of the addition of mercaptans to α,β-unsaturated ketones and esters has been made by Nicolet (10) and others (cf. Mayo and Walling (8)); the addition of mercaptans to azlactones has also been described by Nicolet (9,11) and Carter, Stevens, and Ney (2). These workers found that addition is catalyzed by alkaline reagents such as piperidine and sodium alkoxides. In the present work the addition of benzyl mercaptan to the azlactone of α-benzoylamino-β,β-dimethylacrylic acid (V) proceeded smoothly in anhydrous medium in the presence of sodium methoxide to give S-benzyl-N-benzoyl-β,

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β-dimethylcysteine methyl ester (IV) in good yield. Addition also took place with both the sodium salt of α-benzoylamino-β,β-dimethylacrylic acid (I) and the corresponding methyl ester (II) to give S-benzyl-N-benzoyl-β,β-dimethylcysteine (III) and the corresponding methyl ester (IV) respectively.

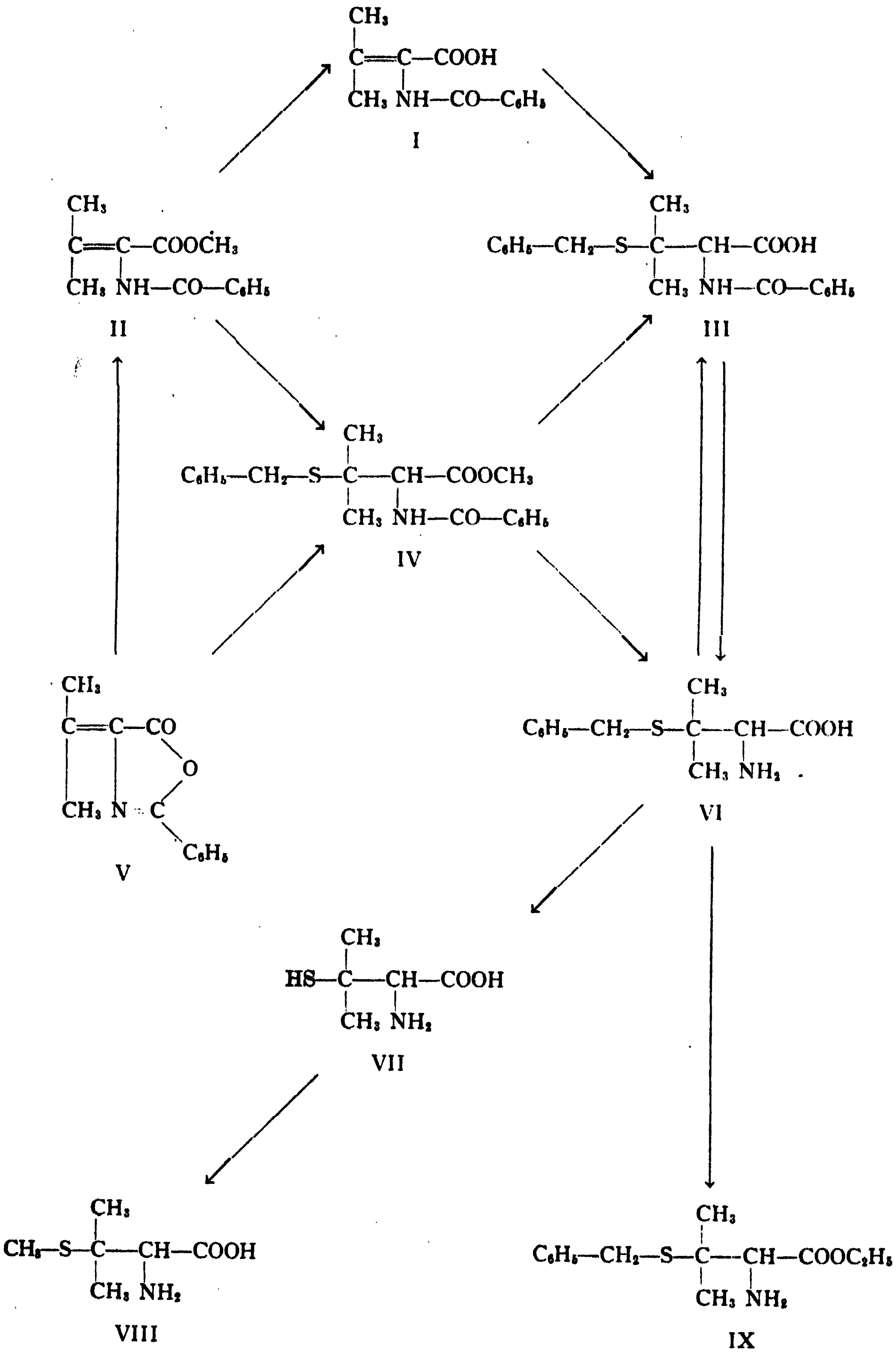
It was found, in the case of addition to the azlactone, that if the conditions cited above were not strictly maintained, or if the purification of the reaction product were delayed (possible prolonged contact with air and moisture), there was isolated from the reaction mixture a considerable quantity of methyl-α-benzoylamino-β,β-dimethylacrylate (II). This compound was also obtained by treating the azlactone (V) with sodium methoxide in anhydrous methanol.

Hydrolysis of S-benzyl-N-benzoyl-β,β-dimethylcysteine methyl ester (IV) to S-benzyl-β,β-dimethylcysteine (VI) could be effected in one or two steps. Because of its insolubility in water, considerable difficulty was encountered in the single step hydrolysis. With most hydrolysing reagents the ester remained unchanged as an oil, even after hours of refluxing, or underwent decomposition; addition of solvents such as alcohol also gave very poor yields. Best results were obtained using a mixture of equal parts of commercial formic acid, concentrated hydrochloric acid, and water (2). Partial hydrolysis with an aqueous mixture of acetic acid and hydrochloric acid gave S-benzyl-N-benzoyl-β,β-dimethylcysteine (III), which, on refluxing with the formic–hydrochloric-acid mixture, gave S-benzyl-β,β-dimethylcysteine (VI). Several derivatives of this compound were prepared, namely, the hydantoin, the ester hydrochloride (IX) and helianthate, and the benzoyl derivative. This last named compound, S-benzyl-N-benzoyl-β,β-dimethylcysteine, was identical with the product obtained by partial hydrolysis of S-benzyl-N-benzoyl-β,β-dimethylcysteine methyl ester (IV).

The replacement of the benzyl group of S-benzyl-β,β-dimethylcysteine (VI) by a methyl group to give the required α-amino acid, S-methyl-β,β-dimethylcysteine (VIII), was accomplished by treating a solution of the above compound in liquid ammonia with sodium according to the method used by du Vigneaud and co-workers (4, 5, 14), and reacting the sodium mercaptide of the corresponding β,β-dimethylcysteine (VII) thus formed with methyl iodide. This hitherto unknown β-thiol-α-amino acid also was isolated as the hydrochloride by precipitation as the water insoluble cuprous mercaptide by means of cuprous oxide (12), followed by decomposition with hydrogen sulphide in dilute hydrochloric acid in the usual manner.

The over-all yield of S-methyl-β,β-dimethylcysteine (VIII), calculated from α-benzoylamino-β,β-dimethylacrylic acid azlactone (V) was 30 to 40% of the theoretical.

It has been found that the β,β-dimethylcysteine inactivates streptomycin, resembling cysteine (3) in this effect. β,β-Dimethylcysteine, when added to the conventional culture medium for the production of penicillin, gave no significant increase in the antibacterial potency of the broth.


I
II
III
IV
V
VI
VII
VIII
IX

Experimental

Methyl α-Benzoylamino-β,β-dimethylacrylate (II)

α-Benzoylamino-β,β-dimethylacrylic acid azlactone (0.40 gm.), prepared according to the directions of Ramage and Simonsen (13), was dissolved in dry benzene (1.6 ml.) and a 5% solution of sodium metal in dry methanol (0.1 ml.) was added. After standing for five minutes crystals appeared; the mixture was then acidified with dilute hydrochloric acid, stirred well, and the crystals collected by centrifuging. Recrystallization from carbon tetrachloride gave white fluffy crystals that sintered at 127° C. and melted at 135 to 136° C. (corrected)*; when mixed with a sample of methyl α-benzoylamino-β,β-dimethylacrylate obtained as a by-product in the preparation of S-benzyl-N-benzoyl-β,β-dimethylcysteine methyl ester, there was no lowering of the melting point.

α-Benzoylamino-β,β-dimethylacrylic Acid (I)

Methyl α-benzoylamino-β,β-dimethylacrylate (5.0 gm., 0.0214 mole) was refluxed in a mixture of concentrated hydrochloric acid (33.0 ml.), glacial acetic acid (110 ml.), and water (65.0 ml.) for one hour. After evaporating *in vacuo* to one-half volume and cooling, the solution deposited colourless crystals, which were filtered and washed with 50% aqueous acetic acid, followed by water. After one recrystallization from ethyl acetate the colourless crystals had a melting point of 215.5 to 216.6° C. (corrected), which was not lowered when they were mixed with an authentic sample of α-benzoylamino-β,β-dimethylacrylic acid prepared from the corresponding azlactone by hydrolysis with sodium hydroxide (1, 13). The yield was 1.8 gm., corresponding to 38% of theory.

S-Benzyl-N-benzoyl-β,β-dimethylcysteine Methyl Ester (IV)

(a) Prepared from α-Benzoylamino-β,β-dimethylacrylic Acid Azlactone (V)

In a dry apparatus consisting of a three-necked flask equipped with mechanical stirrer, dropping funnel, and gas-inlet tube, sodium metal (0.59 gm., 0.0256 mole) was dissolved in anhydrous methanol (125 ml.) and the apparatus filled with dry nitrogen gas and cooled in ice-water. Freshly distilled benzyl mercaptan (15.5 ml., 0.132 mole) was added, followed by a solution of α-benzoylamino-β,β-dimethylacrylic acid azlactone (25.0 gm., 0.124 mole) in dry benzene (125 ml.), added with stirring over a period of one and one-half hours. (The reaction is slightly exothermic, but may be carried out at temperatures ranging from 0° C. to the boiling point with slight variation in yields.) When the addition was complete, stirring was allowed to continue for one hour, after which the mixture was allowed to stand overnight at room temperature. An exact amount of glacial acetic acid was added, equivalent to the weight of sodium used, and the mixture evaporated to dryness *in vacuo* under 5° C. The residue was dissolved in warm dry benzene (70.0 ml.), filtered, and the insoluble sodium acetate washed with benzene. The benzene filtrate and washings were concentrated *in vacuo* to about 100 ml. and petroleum ether (500 ml.) added. The oil that separated crystallized overnight in the cold.

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* *All melting points are uncorrected unless otherwise specified.*

Recrystallized from methanol, the product melted at 66.5 to 67.5° C. (corrected) and weighed 35.0 gm., corresponding to 78.5% of theory. Calc. for $C_{20}H_{23}O_3NS$: C, 67.50; H, 6.49; N, 3.91; S, 8.97%. Found: C, 67.10; H, 6.64; N, 3.86; S, 8.59%.

In several of these runs, where the conditions of the reactions were not rigorously anhydrous, or where the purification of the crude reaction product was delayed, methyl α-benzoylamino-β,β-dimethylacrylate was isolated as by-product. Recrystallized from carbon tetrachloride this product melted at 136.5 to 137.0° C. (corrected) after sintering at 126° C. Calc. for $C_{12}H_{11}O_2N$: N, 5.94%. Found: N, 5.80%.

(b) Prepared from Methyl α-Benzoylamino-β,β-dimethylacrylate (II)

Under the same conditions described in the previous experiment, a solution of methyl α-benzoylamino-β,β-dimethylacrylate (10.0 gm., 0.043 mole) in a mixture (80.0 ml.) of equal parts of methanol and benzene was added to a solution of benzyl mercaptan (5.33 ml., 0.0455 mole) in anhydrous methanol (30.0 ml.) containing sodium metal (0.24 gm., 0.0104 mole).

After standing overnight, the solution was neutralized with glacial acetic acid and the solvents removed *in vacuo*. The residue was dissolved in benzene, filtered, and the reaction product isolated by fractional precipitation with petroleum ether. Three grams of unreacted starting material was recovered and 8.1 gm. of S-benzyl-N-benzoyl-β,β-dimethylcysteine methyl ester was obtained, m.p. 66 to 68° C. The yield was 76% of theory, calculated on the basis of the reacted starting material.

S-Benzyl-N-benzoyl-β,β-dimethylcysteine (III)

(a) Prepared from S-Benzyl-N-benzoyl-β,β-dimethylcysteine Methyl Ester (IV)

S-Benzyl-N-benzoyl-β,β-dimethylcysteine methyl ester (7.14 gm., 0.02 mole) was refluxed for 50 min. in a mixture of glacial acetic acid (60.0 ml.), concentrated hydrochloric acid (18.0 ml.), and water (36.0 ml.), and the resulting solution allowed to crystallize overnight in the cold. The white crystalline product was collected by filtration and washed with aqueous acetic acid; the weight was 4.6 gm., corresponding to 69% of theory. After several recrystallizations from aqueous acetic acid, the S-benzyl-N-benzoyl-β,β-dimethylcysteine melted poorly at 156 to 162° C., after sintering at 151° C. Calc. for $C_{19}H_{21}O_3NS$: C, 66.42; H, 6.18; N, 4.08; S, 9.34%. Found: C, 66.34; H, 6.09; N, 4.28; S, 9.21%.

(b) Prepared from S-Benzyl-β,β-dimethylcysteine (VI)

S-Benzyl-β,β-dimethylcysteine (0.476 gm., 0.002 mole) was dissolved in 2 *N* sodium hydroxide (1.5 ml., 0.033 mole) and water (0.5 ml.), and with stirring, benzoyl chloride (0.43 ml., 0.033 mole) and 2 *N* sodium hydroxide (4.6 ml.) were added simultaneously, and the mixture stirred for 10 min. On acidification with concentrated hydrochloric acid (0.68 ml.) an oil separated which quickly solidified and was filtered. After recrystallization from

50% aqueous acetic acid, 0.50 gm. of S-benzyl-N-benzoyl-β,β-dimethylcysteine was obtained, corresponding to 78% of theory. The melting point was 158 to 163° C., which was not lowered by mixing with a sample of the product obtained in *(a)* above.

S-Benzyl-β,β-dimethylcysteine (VI)

(a) Prepared from S-Benzyl-N-benzoyl-β,β-dimethylcysteine Methyl Ester (IV)

S-Benzyl-N-benzoyl-β,β-dimethylcysteine methyl ester (5.0 gm., 0.014 mole) was refluxed for four hours in a mixture (200 ml.) consisting of equal volumes of 85% formic acid (commercial grade), concentrated hydrochloric acid, and water. The solution was then evaporated to dryness *in vacuo*, and the resulting residue extracted twice with boiling ligroin (65 ml.). The extract was discarded and the residue dissolved in boiling water (70 ml.) and filtered. On adjusting the filtrate to pH 5.8–6.0 a heavy precipitate of S-benzyl-β,β-dimethylcysteine separated; it was filtered and weighed. The yield was 1.8 gm., corresponding to 53% of theory. Recrystallization from water gave white fluffy crystals that melted sharply with decomposition, from 190° C. to 200° C., depending upon the rate of heating. Calc. for $C_{12}H_{17}O_2NS$: C, 60.20; H, 7.16; N, 5.85; S, 13.45%. Found: C, 59.66; H, 6.92; N, 5.53; S, 13.86%.

Later hydrolyses have been carried out using as much as 150 gm. of S-benzyl-N-benzoyl-β,β-dimethylcysteine methyl ester without any decrease in the yield. In these large batches it was found that the crude product resulting from the addition of benzyl mercaptan to α-benzoylamino-β,β-dimethylacrylic acid azlactone could be hydrolysed directly. The substitution of ether for ligroin in the purification of the hydrolysis product gave much better results; in addition to the removal of benzoic acid, all colour and considerable amounts of unreacted S-benzyl-N-benzoyl-β,β-dimethylcysteine ester (which could be recovered) were removed from the final product, the latter requiring but one recrystallization from water to give analytically pure S-benzyl-β,β-dimethylcysteine.

(b) Prepared from S-Benzyl-N-benzoyl-β,β-dimethylcysteine (III)

S-Benzyl-N-benzoyl-β,β-dimethylcysteine (6.40 gm., 0.0186 mole) was refluxed in the hydrolysis mixture described above (90.0 ml.) and the solution treated as in (*a*). After recrystallization from water, 1.6 gm. of S-benzyl-β,β-dimethylcysteine was obtained, corresponding to 36% of theory.

(c) Prepared from α-Benzoylamino-β,β-dimethylacrylic Acid (I)

Metallic sodium (0.470 gm., 0.0204 mole) was dissolved in methanol (30 ml.), and, in an atmosphere of dry nitrogen gas, benzyl mercaptan (2.5 ml., 0.0213 mole) was added. A solution of α-benzoylamino-β,β-dimethylacrylic acid (4.38 gm., 0.020 mole) in methanol (50.0 ml.) was added slowly to the stirred solution and the resulting solution then allowed to stand overnight. Glacial acetic acid (1.15 ml., 0.019 mole) was added and the solvents removed *in vacuo*.

The product, S-benzyl-N-benzoyl-β,β-dimethylcysteine, could not be separated from the starting material by crystallization, so the entire dry reaction residue was refluxed for four hours in a mixture consisting of concentrated hydrochloric acid (95 ml.), 85% formic acid (95 ml.), and water (95 ml.), and the solution evaporated to dryness *in vacuo*. In this hydrolysis any starting material is converted to β,β-dimethylpyruvic acid (13). The dry residue was extracted with boiling ligroin (to remove benzoic acid); the insoluble material was dissolved in dilute hydrochloric acid (80 ml.) and filtered. The filtrate was then adjusted to pH 5.8 and cooled. A small crop of S-benzyl-β,β-dimethylcysteine was filtered and dried; the yield was 20.7 mgm., corresponding to 4% of theory. This compound was identified by melting point, which was not lowered when the compound was mixed with S-benzyl-β,β-dimethylcysteine as prepared in (*a*) above.

S-Benzyl-β,β-dimethylcysteine Hydantoin (5-(β-Benzylthiol-isobutyl)hydantoin)

S-Benzyl-β,β-dimethylcysteine (3.75 gm., 0.015 mole) and potassium cyanate (1.52 gm., 0.02 mole) were refluxed in water (75 ml.) for 45 min. according to the method of Karabinos and Szabo (7). After cooling, the solution was acidified with 10% hydrochloric acid (45 ml). and again refluxed for 30 min. On standing overnight, the solution deposited colourless crystals, which were filtered and dried. Recrystallized twice from ethanol and once from ethyl acetate, the hydantoin weighed 2.6 gm., corresponding to 61% of theory; melting point 204 to 205° C. Calc. for $C_{13}H_{16}O_2N_2S$: N, 10.61; S, 12.14%. Found: N, 10.39; S, 12.32%.

S-Benzyl-β,β-dimethylcysteine Ethyl Ester (IX)

S-Benzyl-β,β-dimethylcysteine (0.50 gm., 0.0021 mole) was suspended in absolute ethanol (25 ml.), cooled in ice-water, and the suspension saturated with dry hydrochloric acid and allowed to stand overnight. After removal of the excess ethanol by evaporation *in vacuo*, the excess hydrochloric acid was removed by standing in a desiccator over solid sodium hydroxide. The dry residue was dissolved in the minimum volume of ethanol and precipitated with dry ether. After several precipitations, 0.63 gm. of the ethyl ester hydrochloride was obtained, corresponding to 95% of theory; the product melted at 157 to 158.5° C., and was very hygroscopic. Calc. for $C_{14}H_{22}O_2NSCl$: N, 4.61%. Found: N, 4.95%.

S-Benzyl-β,β-dimethylcysteine Ethyl Ester Helianthate

S-Benzyl-β,β-dimethylcysteine ethyl ester hydrochloride (0.20 gm., 0.00066 mole) was dissolved in water (2.0 ml.) and treated according to the direction of Gurin and Segal (6) with a hot solution of methyl orange (0.21 gm., 0.000642 mole) in water (5.0 ml.). The reaction was immediate, giving a voluminous bright yellow precipitate of the methyl orange derivative, which after cooling was filtered and washed with a little cold water. Recrystallized from dry methanol, the crystalline helianthate melted at 183 to 183.5° C., with darkening. The yield was 0.232 gm. corresponding to 84% of theory. Calc. for $C_{28}H_{36}O_5N_4S_2$: S, 12.21%. Found: S, 12.27%.

S-Methyl-β,β-dimethylcysteine (VIII)

S-Benzyl-β,β-dimethylcysteine (9.22 gm., 0.04 mole) was placed in a dry 500 ml. flask equipped with a side-arm and mercury-sealed stirrer, and the flask immersed in a dry-ice–alcohol bath. Liquid ammonia (300 ml.), which had been dried by collection over sodium metal, was then allowed to redistill into the reaction flask. With stirring, sodium metal was added in small portions until a total of 2.0 gm., corresponding to 2.5 equivalents, was used. The deep blue colouration of the solution, due to a slight excess of sodium, was then discharged with a small amount of ammonium chloride.

Methyl iodide (6.25 gm., 0.044 mole) was added to the solution, and after a short time stirring was stopped, the flask removed from the dry-ice bath, and the ammonia allowed to evaporate through a soda-lime tube and mercury-trap to prevent the entry of moisture; the last traces of ammonia were removed *in vacuo*. The colourless residue was dissolved in cold water (75 ml.), quickly extracted twice with ether (25 ml.) (to remove dibenzyl), and the aqueous solution quickly brought to pH 5.8–6.0 with concentrated hydrochloric acid, and cooled. The white crystals that separated were filtered and washed with cold water; concentration and cooling of the filtrate yielded a second crop of crystals.

Recrystallization of the crude product from water gave 6.1 gm. of pure S-methyl-β,β-dimethylcysteine corresponding to 96% of theory. The melting point varied with the rate of heating; the sample used for analysis melted at 254 to 256° C. Calc. for $C_6H_{13}O_2NS$: N, 8.59; S, 19.65%. Found: N, 8.46; S, 19.60%.

β,β-Dimethylcysteine Hydrochloride (VII)

S-Benzyl-β,β-dimethylcysteine (4.76 gm., 0.02 mole) was added to anhydrous liquid ammonia (300 ml.) contained in a dry flask equipped with a mercury-sealed stirrer and cooled in a dry-ice–alcohol bath. To this mixture metallic sodium (1.098 gm., 0.047 mole) was added in small pieces, until an excess was indicated by a blue colouration lasting 5 to 10 min. The solution was decolorized by the addition of a small amount of ammonium chloride. The liquid ammonia was then allowed to evaporate through a mercury trap, the latter to prevent air oxidation.

The residue was dissolved in water (20 ml.), and the resulting solution cooled, and treated with concentrated hydrochloric acid (2.5 ml.). The solution was then extracted with ether to remove dibenzyl, and evaporated to dryness *in vacuo* under an atmosphere of nitrogen, the temperature being kept below 45° C. The residue was dissolved in water (50 ml.), and an excess of freshly prepared cuprous oxide was added with vigorous stirring. The suspension was adjusted to pH 4.0, diluted with water (600 ml.), and stirred for an additional two hours. The insoluble cuprous mercaptide, containing excess cuprous oxide, was centrifuged and washed twice with cold water, after which it was suspended in water (300 ml.) containing concentrated hydrochloric acid (3.0 ml.) and saturated with hydrogen sulphide. When the decomposition was complete, the copper sulphide was removed by centrifuging, washed several times with water, and the combined filtrate and washings were evaporated to dryness *in vacuo* in an atmosphere of nitrogen. The dry solid consisted of pure β,β-dimethylcysteine hydrochloride. The yield was 3.54 gm., corresponding to 92% of theory. Calc. for $C_5H_{11}O_2NS$. HCl: C, 32.30; H, 6.47; N, 7.55; S, 17.25; Cl, 19.10%. Found: C, 32.69; H, 6.89; N, 7.58; S, 17.32; Cl, 19.45%.

β,β-Dimethylcysteine hydrochloride gave positive ferric chloride, ninhydrin, and nitroprusside tests.

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ON THE SPECIFICITY OF DYE TITRATION FOR ASCORBIC ACID[1]

By Jules Tuba[2], George Hunter[3], and Helen Ruth Steele[4]

Abstract

The 2,6-dichlorophenolindophenol method of assay of vitamin C has been critically examined with respect to a number of fresh, boiled, and otherwise treated plant materials. Comparative values are given for ascorbic acid as determined by the usual method, for non-vitamin C reductants, and for dehydroascorbic acid.

In the fresh uncooked materials examined, non-vitamin C reductants were not found and only in cabbage, peas, and pigweed leaves did dehydroascorbic exceed 10% of the ascorbic acid value.

Boiling produced significant amounts of non-vitamin C reductant in cabbage and peas.

In rose hips the dye titration gives an accurate measure of ascorbic acid. The amounts of dehydroascorbic acid and non-vitamin C reductant, even under storage at room temperature for over a year, are insignificant.

It is concluded that the 2,6-dichlorophenolindophenol method of assay of vitamin C is highly specific but in the case of certain cooked foodstuffs non-vitamin C dye reductants may, without check by other methods, introduce significant errors.

Introduction

Birch, Harris, and Ray (2) in their parallel chemical and biological assays of a wide variety of plant and animal materials dispelled much of the confusion that previously existed on the subject of the specificity for vitamin C of the Tillmann's titration with the redox indicator 2,6-dichlorophenolindophenol. Cysteine was the only substance that might be found in biological material observed by these workers to reduce the dye under the conditions employed. They concluded that the titration method gives accurate results for vitamin C in a wide variety of animal and vegetable materials.

During the last few years the specificity of the dye titration has been called in question from a number of directions. The increase in titration value sometimes found after cooking, the suggested presence of "combined ascorbic acid" (6), the occurrence of dehydroascorbic acid in fresh and stored fruits and vegetables, are all problems that have been exhaustively investigated by Harris and Olliver (3), with the conclusion that the dye titration "can be recommended with confidence for all ordinary routine analyses of plant materials, as giving the total anti-scorbutic activity".

Since the above general conclusion was formulated, observations of non-vitamin C reductants of 2,6-dichlorophenolindophenol compel the attention of those using this dye for the assay of the vitamin.

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Mapson (7) has shown, by use of the formaldehyde method of Lugg (5), that in fresh fruits and vegetables, and in various preserves of these, the dye titration is usually better than 90% due to the ascorbic acid, but in certain dried vegetables, particularly those with a high sugar content and stored at temperatures over 25° C., there may be no ascorbic acid present when the direct dye titration would indicate as much as 93 mgm. per 100 gm. Mapson believes that some of these non-vitamin C reductants are reductones.

The possible occurrence of reductones and related substances has been studied by Wokes and his associates (12), who (13) coined the current misleading term, "apparent vitamin C", to include such substances and others that reduce the dye but possess no antiscorbutic activity.

Various methods, including Lugg's, have been used to differentiate ascorbic acid from such reductants. The method of Levy (4), depending on the fact that ascorbic acid does not reduce the dye in 20% hydrochloric acid solution, while a gluco-reductone solution does, is the only one in addition to Lugg's that we are concerned with here. Levy's method indicates that nearly 20% of the usual dye titration in fresh orange juice is traceable to non-vitamin C reductant(s).

Although there is yet great discrepancy in the observations of different workers on the subject, the trend of the evidence is that non-vitamin C reductants may give rise to considerable error in the usual dye titration in certain foodstuffs that have been dried, baked, or stored for long periods at fairly high temperatures. The work of Wokes and his associates would indicate that there may be appreciable non-vitamin C reductants in certain fresh fruits, particularly green walnuts.

We were led to the present investigation primarily from our interest in rose hips. It seemed that the very high assay given by the dye method in this material should be checked from every possible angle. A biological assay has already been reported (9) showing that the reduction of 2,6-dichlorophenolindophenol by rose hip powder is due wholly to ascorbic acid. In addition, in a paper (10) that accompanies this one, we describe the isolation of ascorbic acid from rose hips as quantitatively as might be expected. We here report our observations on the question of non-vitamin C reductants in relation to the 2,6-dichlorophenolindophenol titration on rose hip preparations and certain other fruits and vegetables. The place of dehydroascorbic acid is also considered.

Experimental

I. *Non-vitamin C Reductants*

The formaldehyde method of differentiating non-vitamin C reductants from vitamin C was first developed by Lugg (5) and later modified by Mapson (7) and by Wokes *et al.* (14). The basis of the use of formaldehyde is, according to Lugg, the fact that at pH 3.5, ascorbic acid will condense readily with formaldehyde, thus becoming non-reducing towards 2,6-dichlorophenolindophenol, while reductones do not combine with formaldehyde at this pH.

Mapson found, however, that there is no pH at which formaldehyde condenses with ascorbic acid without some condensation occurring simultaneously with non-vitamin C reductants. He recommends pH 2, for while the condensation with vitamin C occurs more slowly, the reaction with non-vitamin C reductants proceeds to a lesser degree than at higher pH values such as 3.5. Wokes suggests pH 4.5 for the condensation. While there seems to be general agreement about certain details of the formaldehyde method, such as the optimal concentration of formaldehyde to be used, it was felt necessary to determine which of the various suggested pH values should be chosen for our work.

We followed the rate of condensation of formaldehyde with ascorbic acid alone and, similarly, with "gluco-reductone" solution prepared by the method of Mapson (7). The results in Fig. 1 indicate that 2 is the most desirable pH value to use. In this matter, as in most details of the formaldehyde treatment of material being assayed for non-vitamin C reductants, we have adhered to the method outlined by Mapson, with the titration temperature maintained at 20° C.

Mixtures of ascorbic acid and gluco-reductone were treated with 8% formaldehyde at pH 2.0. Aliquots were titrated, for the first 20 min., at 5 min. intervals and subsequently at 10 min. intervals, up to 120 min. The titration curve is shown in Fig. 2. It will be seen that ascorbic acid is condensed with formaldehyde in 50 to 60 min., and after that the reaction with reductone, which is much slower, gives a linear curve. If the linear part of the curve is then extrapolated to zero time, the value of the intercept on the axis, representing the original amount of the reductone present, should, on subtraction from the total titration at zero time, give the amount of ascorbic acid that was originally present in the mixture of ascorbic acid and reductone. The amount of ascorbic acid calculated from the curve in Fig. 2 agrees to within 1.2% of the amount actually added to the mixture.

Similarly, model experiments were carried out using the differential titration method of Levy (4). To a solution of gluco-reductone, ascorbic acid was added to a concentration of 0.1 mgm. per ml. (*a*) Titration of the mixture gave the dye equivalent of both ascorbic acid and gluco-reductone, since under these conditions both substances reduce the dye. (*b*) To an aliquot of the mixture 36% hydrochloric acid was added in the ratio of 2 parts of solution to 2.5 parts of acid to give a final concentration of 20% hydrochloric acid. Under these conditions, Levy states, ascorbic acid is in its keto form, and will not react with the dye, although the reductone will. Hence titration of this second solution gives the amount of the non-vitamin C reductants. (*c*) An aliquot of (*b*) was diluted with five volumes of water making keto-enol tautomerization again possible. As a result ascorbic acid as well as the gluco-reductone was able to reduce the dye, and a dye equivalent equal to (*a*) was

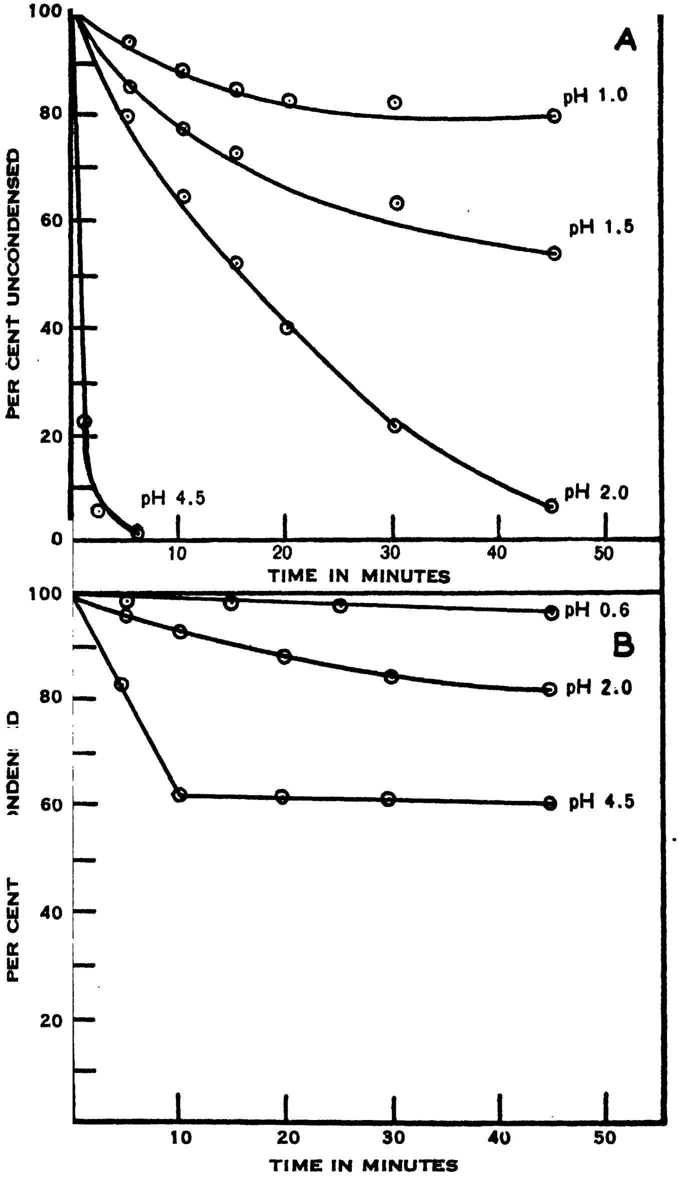

FIG. 1. *The effect of pH on the rate of condensation of formaldehyde with (A) ascorbic acid and (B) gluco-reductone. Temperature, 20° C.*

obtained. The results of the experiment are summarized below and are given in terms of 1 ml. of (*a*), the original solution, containing ascorbic acid = 0.100 mgm. per ml. and gluco-reductone = 0.336 mgm. per ml.

(*a*) Dye equivalent = 0.436 mgm. per ml. reducing substances.
(*b*) Dye equivalent = 0.325 mgm. per ml.
(*c*) Dye equivalent = 0.436 mgm. per ml.
$a - b$ = 0.111 mgm. of ascorbic acid, or an error of 11.0%.

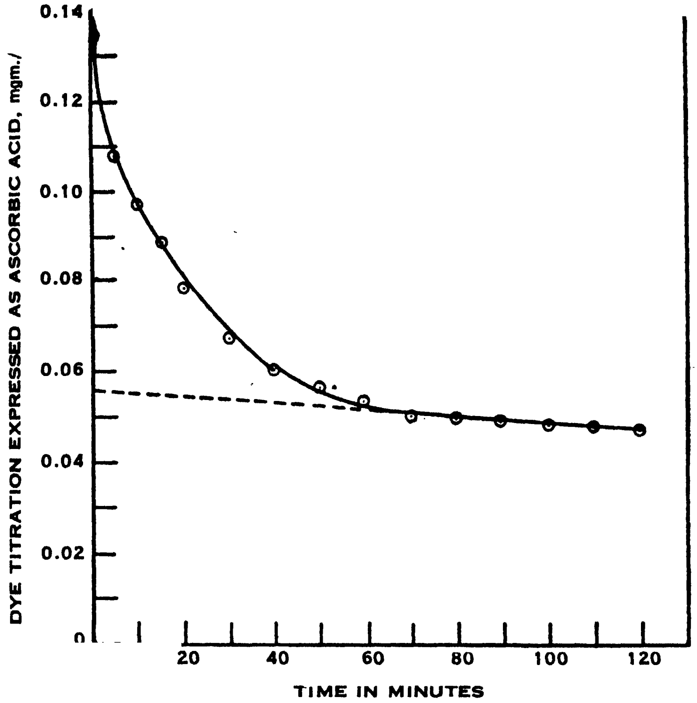

FIG. 2. *Reaction of 8% formaldehyde at 20° C. and pH 2.0 with a solution containing 0.0775 mgm./ml. ascorbic acid and 0.0568 mgm./ml. gluco-reductone. Ascorbic acid found by extrapolation to zero time = 0.1344 − 0.056 = 0.0784 mgm./ml. Error = 1.2%.*

This experiment indicates that it is possible by the method described by Levy to determine with fair accuracy the amounts of ascorbic acid and gluco-reductone in mixtures of the two substances.

ASSAYS OF PLANT MATERIALS

(*a*) *Formaldehyde Method of Mapson* (7)

The assay material is extracted with 5% metaphosphoric acid to give a final concentration of approximately 0.1 mgm. ascorbic acid per ml. or its equivalent in dye reducing substances. The indophenol titration value of the extract is determined and an aliquot is set in the dark for one hour. A decrease of the titration value by the end of that time is due to the presence of dihydroxymaleic acid or certain other compounds found in malt, etc. (7). (This did not occur with any of the materials assayed by us.)

The main part of the extract is brought to pH 2.0 by the addition of sodium citrate and kept at 20° C. for the duration of the determination. An aliquot is titrated, and this value, corrected for the dilution due to formaldehyde, and expressed as ascorbic acid in mgm. per ml. is the initial value at zero time on the graph.

Formaldehyde (36%) is added to the solution to a final concentration of 8%. Aliquots are taken at five minute intervals for 20 min. and titrated immediately. Thereafter titrations are made every 10 min., generally for another 90 to 100 min. The values of the titrations with 2,6-dichlorophenol-indophenol, expressed in mgm. of ascorbic acid per ml., are plotted against time as the abscissa. The linear part of the curve is extrapolated to the ordinate, and the value thus obtained is that of the non-vitamin C dye reductants in mgm. per ml. (Fig. 3, *A* and *B*).

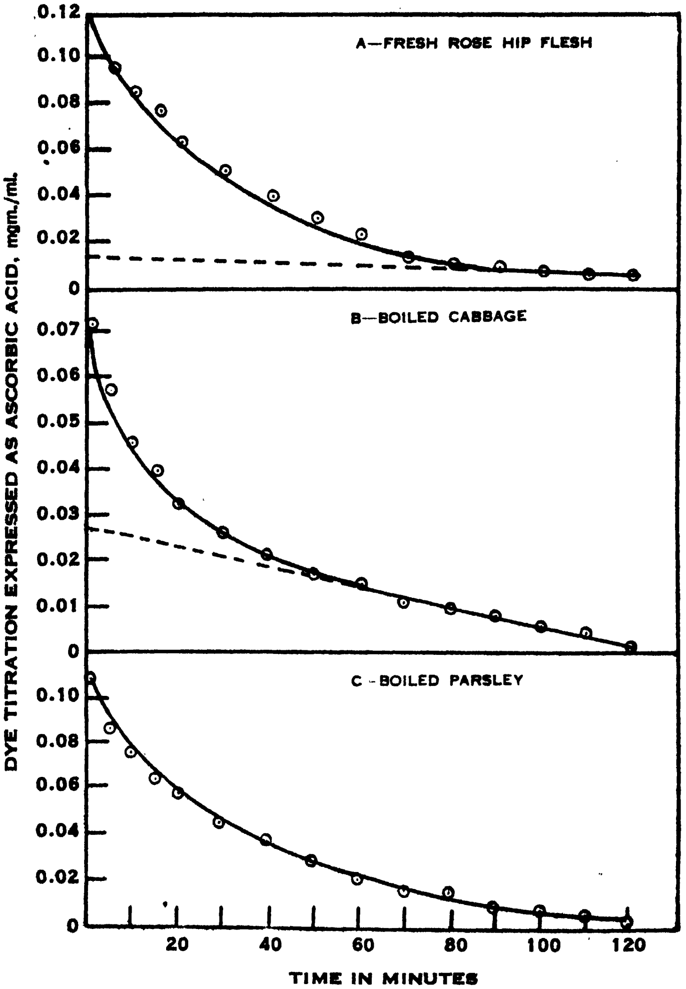

FIG. 3. *Estimation of non-vitamin C reductants by the formaldehyde method in (A) fresh rose hip flesh, (B) boiled cabbage, and (C) boiled parsley.*

One of our chief criticisms of the formaldehyde method, in addition to the time required, is, that while the linear region of the curve is very distinct with model experiments using simple mixtures of ascorbic acid and glucoreductone (Fig. 2), in many cases it is by no means so definite in assays of plant materials. As a result the slight variations possible in the slope of this part of the curve (Fig. 3, *C*) will make very appreciable differences in the value of the intercept on the ordinate.

(*b*) *Differential Titration Method of Levy* (4)

The assay material is extracted with 5% metaphosphoric acid in the usual manner. Aliquots are titrated as described to get the combined value of the ascorbic acid and the non-vitamin C reductants. To a portion of the extract 2.5 parts of concentrated hydrochloric acid is added for every 2 parts of the metaphosphoric extract, and the dye equivalent of the solution gives the value of the non-vitamin C reductants. Part of the strong acid solution is diluted with five volumes of water and the reduction of the dye by this solution is due to both vitamin C and non-vitamin C reductants. The first and last titration values should check. Subtraction of the second titration value gives the concentration of ascorbic acid. Results by this method are shown in Table I.

This method has a time saving advantage over the formaldehyde estimation. After the addition of concentrated hydrochloric acid the extract must be titrated at once, otherwise the titration value will alter markedly. In some cases the addition of the concentrated hydrochloric acid turns the extract brown, masking the titration end-point. This occurred in the assay of white currant jelly, where the result by the Levy method differed greatly from the formaldehyde method. Further, the Levy method is not satisfactory with coloured extracts requiring the McHenry and Graham method of titration (6), owing to the rapid fading in the chloroform layer of the pink colour marking the end-point.

II. *Dehydroascorbic Acid*

The amount of the oxidized form of vitamin C in plant material we determined by three different methods. The first of these is that used by Waagen and Pett (11), which consists simply in adding powdered zinc to the acid extract. The difference in titration before and after adding the zinc was considered by Waagen and Pett to be a measure of the amount of dehydroascorbic acid. The second is the commonly used hydrogen sulphide method devised by Bessey (1). Finally, we used the more recent 2,4-dinitrophenylhydrazine method of Roe (8). Apart from being an independent colorimetric method for dehydroascorbic acid, Roe's method has the added advantage that thiourea stabilizes ascorbic acid. It should be noted that Roe considers that the indophenol titration is reliable if dehydroascorbic acid is measured also. He limits the possible interference of reductones to those foods that have been cooked at alkaline pH's because he finds that these interfering substances do not form at acid or neutral reactions.

Discussion

Table I shows comparative values obtained for ascorbic acid by the usual dye titration, non-vitamin C reductants determined by the Mapson and the Levy methods, and dehydroascorbic acid as determined by reduction with

TABLE I

COMPARATIVE ANALYSIS OF PLANT MATERIALS FOR ASCORBIC ACID, NON-VITAMIN C REDUCTANTS, AND DEHYDROASCORBIC ACID. UNLESS OTHERWISE INDICATED ASSAY MATERIAL IS FRESH

Material	Ascorbic acid by dye titration, mgm./100 gm.	Non-vitamin C reductants, % of indophenol value		Dehydroascorbic acid, mgm./100 gm.		
		Mapson	Levy	Zinc	Bessey	Roe
Black currants	156.6	0.0	—	25.7	26.8	3.1
Black currant jelly	19.0	6.2	—	—	—	—
Broad beans	10.9	0.0	—	2.7	5.7	1.5
Broad beans, boiled	25.3	0.0	—	1.7	1.2	4.0
Cabbage, sample No. 1	84.9	0.0	—	−30.0	7.5	13.6
Cabbage, boiled, sample No. 1	40.9	20.0	—	−24.3	1.1	3.1
Cabbage, sample No. 2	58.3	0.0	—	−18.4	0.0	9.1
Cabbage, boiled, sample No. 2	38.9	36.0	—	−23.7	2.2	5.7
Cherry plum	0.12	—	—	2.6	2.3	5.0
Cherry plum, boiled	4.4	10.0	—	2.7	5.1	1.9
Guava	87	0.0	0.0	—	—	—
Hazel nut leaves	394.8	2.0	—	13.5	16.2	—
Parsley	315.0	5.0	—	0.0	18.7	16.8
Parsley, boiled	233.3	14.0	—	0.0	6.2	23.5
Parsley, dried	832.0	—	6.0	—	—	—
Peas, sample No. 1	0.4	—	—	22.8	—	20.0
Peas, sample No. 2	0.7	—	—	24.3	—	—
Peas, sample No. 3	2.7	—	—	6.1	—	—
Peas, boiled, sample No. 2	19.8	14.0	—	4.5	3.4	3.1
Peas, boiled, sample No. 3	17.3	15.0	—	1.1	1.5	2.7
Pigweed leaves	275.4	0.0	—	0.0	0.0	—
Pigweed leaves, dried	385.0	0.0	—	27.0	—	53.5
Raspberries	22.4	0.0	—	1.6	1.5	2.5
Raspberry jam	2.7	22.0	—	—	—	—
R. acicularis dried powdered flesh (freshly prepared)	4925	8.0	6.0	0.0	0.0	102.5
R. acicularis dried powdered flesh (stored 16 months)	2902	—	5.0	—	—	—
R. laxa hip flesh	4950	4.0	—	—	—	—
R. woodsii hip flesh	2056	5.0	—	0.0	0.0	26.0
R. woodsii hip flesh	1890	0.0	—	0.0	0.0	18.0
R. woodsii hip flesh	1802	—	6.0	—	—	—
R. woodsii hip flesh	2184	—	2.5	—	—	—
R. woodsii flesh, boiled	2052	6.0	—	0.0	0.0	3.1
Rose hip and crab jelly	245.5	4.0	—	0.0	0.0	0.0
Rose hip and crab jelly	236	12.8	7.5	0.0	0.0	0.0
White currants	64.8	0.0	—	1.3	2.3	5.0
White currant jelly	8.2	—	65.0	—	—	—
White currant jelly	2.3	30.0	—	—	—	—

zinc, with hydrogen sulphide, and by the colorimetric method of Roe. Fresh, cooked, and otherwise processed plant materials were used.

The method of Levy became available only in the later stages of our work so that comparatively few materials were assayed by it. Our few results indicate that the Mapson and Levy methods give values for non-vitamin C reductants of about the same magnitude.

In the materials examined by us, however, it is only in exceptional cases that the non-vitamin C reductant values appear significant. In all fresh materials tested the non-vitamin C reductant values are zero or negligible. These observations are in accord with those of Harris and his colleagues.

Increase in titration value as a result of boiling is seen especially in the case of broad beans and peas. In the case of beans the increase after boiling is not accompanied by any shift in the values for dehydroascorbic acid nor for non-vitamin C reductant. In the cases of peas the increase is largely accounted for by the appearance of non-vitamin C reductant and an almost corresponding drop in dehydroascorbic acid. Our data on this point, however, are too few to do more than suggest further investigation.

Our results for dehydroascorbic acid by the three methods used are very erratic. With the exception of rose hips there is a measure of concordance between the method of Bessey and that of Roe, but it is not such as to inspire much confidence. On the assumption that the Roe method gives a fair estimate of dehydroascorbic acid, only in the case of fresh cabbage, peas, and pigweed leaves does dehydroascorbic acid exceed 10% of the ascorbic acid. In dried rose hip powder dehydroascorbic acid by one observation amounts to about 2% of the ascorbic acid present. So we may conclude that rose hips contain no significant amounts of either dehydroascorbic acid or of non-vitamin C reductants even after long storage at room temperatures.

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ISOLATION OF ASCORBIC ACID FROM ROSE HIPS[1]

By Jules Tuba[2] and George Hunter[3]

Abstract

A method has been described for the isolation of ascorbic acid from rose hips.

Introduction

Our bio-assay (5) proved that the material in rose hips that reduces 2,6-dichlorophenolindophenol is ascorbic acid. In accordance with this finding is our evidence (7) of the absence of non-vitamin C reductants. Conclusive proof that rose hips are a rich source of vitamin C is now furnished by its isolation.

The high concentration of the vitamin in rose hips might suggest that its isolation should be a simple matter. It has proved otherwise.

The methods successfully used by Szent-Györgyi for its isolation from adrenal tissue, cabbage, and orange (4), and from red pepper (3), are not fitted to separate ascorbic acid from other constituents of rose hips. Likewise the method used by Waugh and King (9) to prepare the vitamin from lemon juice, the method used by Bauman and Metzger (1) for iris leaves and skunk cabbage leaves, and the method of Bukin and Garkina (2) for green walnuts failed to yield any crystalline vitamin when applied to rose hips. We had no difficulty in preparing ascorbic acid from iris leaves by Bauman and Metzger's method.

It required considerable work to overcome the main difficulties in the preparation. We were guided to some extent by our study (6) of the approximate nutrient composition of rose hips. The presence there shown of relatively large amounts of fermentable sugars necessitated either a destruction of these by yeast, or precipitation of the ascorbic acid as a lead salt. In concentrations of the order of 1 mgm. per ml. the lead salt of ascorbic acid begins to precipitate near pH 5.0 and is completely precipitated at pH 7.8. The lead salts of glucose and fructose, even in considerably higher concentration, do not precipitate until the pH greatly exceeds 8.0. By fermenting away the reducing sugars we have succeeded in preparing crystalline ascorbic acid from rose hips without fractionation as lead salt, but it is simpler to dispense with fermentation and use the lead salt in the pH range indicated above.

Separation from the fermentable sugars is, however, a minor difficulty in the preparation from rose hips. If rose hips are treated with aqueous barium acetate as described by Szent-Györgyi for red peppers, and lead acetate added

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to the filtrate, an enormous lead precipitate is obtained in the usual pH range. When the lead is removed from this material, subsequent fractionation by means of solvents is futile.

Aqueous extracts from hips contain large amounts of a pectin-like material that precipitates as a lead salt in the ascorbic acid pH range. Much of this material can be removed by preliminary treatment with methanol with negligible loss of ascorbic acid. In the subsequent lead salt, however, there still remains considerable non-ascorbic acid material but this can be fairly readily removed by solvent fractionation.

Bauman and Metzger add lead acetate to a final concentration of 25 to 30%. This is quite unnecessary and, indeed, in the case of rose hip material detracts from the value of the lead fractionation. By using the minimum necessary amount of lead acetate the specificity of the lead fractionation is enhanced.

The necessary amount of lead acetate for a particular batch is quite easily determined in the following way. An estimate of the ascorbic acid in solution is made by titration of a small aliquot portion. A solution of lead acetate is added to give a weight of lead acetate trihydrate about six times that of the ascorbic acid present in the solution. This suffices for a simple aqueous solution of ascorbic acid, as arbitrarily tested by adding an excess of ammonia, centrifuging, and proving the absence of ascorbic acid by dye titration on the acidified supernatant fluid. With rose hip extracts some three to five times this amount of lead acetate may be necessary, but the precise amount can be determined with a few trials on small aliquot portions as above indicated.

The preparation may now be described.

Preparation

Material

Ripe rose hips were just covered with water and boiled till soft. They were stirred and crushed to a mixture of pulp and seeds. The seeds were separated by passing through a sieve and the resulting "puree" was transferred to beer bottles, sterilized, and capped. This material, resembling thin tomato catsup, was stored for over a year without loss of vitamin. It usually contained 3 to 4 mgm. of ascorbic acid per ml. and served as our starting material for the preparation.*

Five hundred millilitres of puree (1400 mgm. of ascorbic acid) was reduced *in vacuo* to a paste (without crusting on the sides of the flask). Absolute methanol was added with shaking until no more appreciable precipitation took place (four to five volumes). The material was filtered through a Büchner. The filtrate was reduced *in vacuo* to a small volume, while the residue on the Büchner was resuspended in methanol and again filtered. The washing was repeated and the two last filtrates added to the thin syrup

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** Although our work was done chiefly with such purees, we were able to isolate crystalline ascorbic acid from dried, powdered rose hip flesh, containing 3.5 to 5.0% of ascorbic acid. Such material was extracted and washed twice with methanol, and the extract and washings were treated as in the case of the puree.*

from the first filtrate. A further precipitate appears here and is removed. The filtrate is reduced *in vacuo*, the residue dissolved in water, and made to one litre volume (1200 mgm. of ascorbic acid).

Glacial acetic acid is added to the solution to pH about 3.5. The predetermined amount of 40% lead acetate* (60 ml.) is added and the solution mixed. Its pH will now be near 4.5. The precipitate is removed, washed, and discarded (with loss of about 50 mgm. of ascorbic acid). To the filtrate strong ammonia is added to pH 7.8, the precipitate collected in centrifuge bottles, and the supernatant fluid and washings are discarded (with loss of about 50 mgm. of ascorbic acid).

Crushed ice is added to the precipitate in a 250 ml. centrifuge bottle and the precipitate stirred to a smooth thick paste, in presence of ice.

Ten per cent sulphuric acid is added until the solution gives a clear blue test with Congo red paper; the end-point is checked with barium chloride.

The lead sulphate precipitate is removed, the filtrate collected, and an aliquot titrated (905 mgm. of ascorbic acid).

The solution is reduced *in vacuo* to a thick syrup. It is dissolved in a minimum amount of anhydrous methanol with warming. Then five volumes of anhydrous acetone is added gradually with shaking and cooling. Much of the gummy precipitate adheres to the flask and the rest is centrifuged. The precipitates are dissolved in a minimum amount of methanol in the centrifuge bottles. This is transferred to dissolve the main bulk in the flask. Five volumes of acetone is added. The resulting gum may be treated again with methanol and acetone: usually two such washings are sufficient to remove almost all of the vitamin.

The methanol–acetone extract and washings are combined and reduced to a small volume *in vacuo*. The syrup thus obtained is dissolved in a minimal amount of methanol and 10 volumes of acetone is added. The precipitate is again washed twice with methanol and acetone. The combined methanol–acetone extract and washings are again reduced *in vacuo* to a syrup.

The syrup obtained after the above fractionation with methanol and acetone is dissolved in the least amount of anhydrous methanol. Then 10 volumes of anhydrous acetone is added and finally 10 volumes of anhydrous petroleum ether. There is formed a large amount of oily precipitate, some of which remains suspended in the supernatant liquid, and is separated by centrifugation. The oily precipitate formed at this step tenaciously holds the vitamin, and the procedure has to be repeated six to eight times with methanol, acetone, and petroleum ether in the above ratio, to get nearly quantitative recovery (at this stage 850 mgm. of ascorbic acid).

** A 5 ml. aliquot is removed, 0.1 ml. of 40% lead acetate added and, after mixing, ammonia is added until the solution is alkaline to phenolphthalein. The mixture is centrifuged and 1 ml. of the acidified supernatant fluid is titrated with standard dye. If there is an appreciable titration another 5 ml. aliquot is tested with 0.2 ml. of 40% lead acetate and the procedure repeated until there is a negligible titration.*

The syrup remaining after the fractionation with methyl alcohol, acetone, and petroleum ether is dissolved in a small amount of acetone and transferred to a boiling-tube. The tube is then evacuated until much of the acetone is removed and the syrup is moderately thick. The evacuated tube is placed in an ice–salt mixture. Crystallization may start at once, and is allowed to continue for one to two days. The crystals are filtered off and washed in cold anhydrous acetone. Yield; 560 mgm. acetone derivative or 456 mgm. ascorbic acid or 33% of that originally present. Crude product: melting point, 193° to 195° C. $[\alpha]_D^{20°}$, in absolute ethanol = + 13. The corresponding values recorded by Vargha (8) for the monoacetone derivative of ascorbic acid are 220° to 222° C. and + 15.

The dye titration yielded values corresponding to the composition of the monoacetone derivative.

The crude and slightly brown monoacetone derivative was dissolved in water and boiled with a little charcoal. The filtrate was dried in a vacuum desiccator and the residue recrystallized from ethanol.

The crystals are proved to be ascorbic acid by the following properties.

Melting point, 182° to 186° C. (Authentic, 184° to 186° C.)
$[\alpha]_D^{20°}$, in water, + 21 (Authentic, + 22.5)
$[\alpha]_D^{20°}$, in absolute ethanol, + 57 (Authentic, + 58.7)

Remarks

From our experience in various preparations we believe that, for all practical purposes, all the dye reducing power of rose hips is attributable to ascorbic acid.

From the boiled pulp the reducing material is quantitatively extractable by water and methyl alcohol so that we can conclude the vitamin is "free" in the tissue. At no stage in the preparation was there any ground for supposing the presence of any non-vitamin C reductant.

Appreciable loss in the course of any preparation of vitamin C without recourse to maintaining anaerobic conditions is to be expected. At certain stages in the method described above there can be great losses if adequate precautions are not taken. In the initial stage, there is fairly rapid destruction of the vitamin in aqueous methyl alcohol solution and the "puree" extract should be reduced to the gum stage as quickly as possible. The syrups or gums can be kept almost indefinitely without loss of vitamin.

The other stage at which there can be great loss of the vitamin is in freeing it from its lead salt. The sticky lead precipitate is hard to disperse in cold water and recourse to violent shaking, after the addition of some sulphuric acid, incorporates oxygen with resultant destruction of the vitamin, especially perhaps in presence of traces of catalyst, like copper.

In the subsequent solvent fractionation there is little destruction of the vitamin. Losses that do occur are traceable to incomplete washing of residues.

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THE HEAT CAPACITY OF AQUEOUS SOLUTIONS OF HYDROFLUORIC ACID[1]

BY T. THORVALDSON[2] AND E. C. BAILEY[3]

Abstract

The heat capacity of aqueous solutions of hydrofluoric acid varying in concentration from 0.55 to 48% was determined over the temperature range 18° to 20° C. The respective values for the specific heat varied between 0.996 and 0.718 cal. per gm. The values obtained are consistent among themselves but differ markedly from those found in the literature. The apparent molal heat capacity of the solute over this range of concentration and temperature was calculated and compared with values obtained from the data of other experimenters.

In connection with experimental determinations of the heats of formation of the aluminates and silicates of calcium, the authors found it necessary to determine the heat capacities of systems composed mainly of aqueous solutions of hydrofluoric acid over the temperature range 18° to 20° C. Calculations of the specific heats at 19° C. of solutions of hydrofluoric acid from these data gave values that differed considerably from those found in the literature (4, 6, 7). A series of determinations over a wide range of concentrations was therefore undertaken. The values obtained for solutions varying from 0.55% ($HF \cdot 200\ H_2O$) to 48% ($HF \cdot 1.20\ H_2O$) hydrofluoric acid are given below. The energy measurements were made in international joules and converted to defined calories by dividing by 4.1833.

Apparatus, Experimental Procedure, and Materials

The calorimeter system was of the adiabatic type, the copper submarine vessel enclosing the calorimeter being immersed in a large cylindrical tank, the temperature of which could be easily controlled by additions of hot or cold water with rapid mechanical stirring. The hydrofluoric acid was contained in a cylindrical vessel of fine gold, capacity about 750 cc., resting on inverted T-shaped ebonite supports and insulated from the copper submarine container by an air space about 6 mm. wide. The inside of the submarine vessel was coated with paraffin. The acid was stirred at a rate insuring temperature uniformity by a rotary stirrer (of an alloy 80% gold + 20% copper) thermally insulated from its shaft by a thin ebonite rod and operated

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by a small synchronous motor. The heating of the acid was effected by a small heater coil, of No. 34 constantan wire wound on a mica cross as described by Meyers (3), enclosed in a sealed nitrogen-filled platinum tube. The leads, made of No. 18 copper wire (No. 32 for portion inside calorimeter), were shielded against leakage currents. The heater system (resistance of coil about 50 ohms) was suspended by means of an ebonite tube through which the leads passed. Lead accumulators of large capacity and very constant voltage were used as the source of current.

The wiring of the potentiometer system was similar to that described by White (9, pp. 134-135), using standard resistances of 0.1 and 10 ohms calibrated by the U.S. Bureau of Standards, a type K Leeds and Northrup potentiometer, a sensitive galvanometer, and a calibrated Weston cell, making possible the measurement of both the current through the heater and the voltage across the heater at one setting of the potentiometer. The Weston cell was frequently compared with another calibrated cell. All the electrical equipment was placed on an equipotential shield.

The length of the heating period was measured by means of a stop watch, calibrated against a chronometer, the spring of the stop watch always having the same tension at the beginning of a run. The current was run through an external resistance of about 50 ohms for a 10 min. period before switching over to the calorimetric heater. Potentiometric readings were taken every minute during the run and the values obtained averaged. The usual heating period was about 12 minutes.

The temperature rise was measured by means of a Beckmann thermometer graduated in 0.01° C., calibrated by the U.S. Bureau of Standards, and readings were easily estimated to 0.001° C. The relative calibration corrections over the range used were very small (± 0.001° C. from the mean). Corrections were also made for setting and for exposed stem. The temperature of the outside bath was read by means of a similar thermometer. The thermometer exposed to the acid was protected by a closely fitting sheath of thin platinum foil, with any space between the platinum and the glass filled with mercury. During a run, the temperature of the outside bath was maintained at 0.010° C. above the temperature of the liquid in the gold calorimeter vessel. Transfer of heat due to this head was automatically included in the correction for stirring ("rating"), which was determined for at least one-half hour before and after each run. The temperature of the room varied only slightly during the whole series of experiments.

The "electrical energy equivalent" of the calorimeter was obtained by a series of nine determinations (made over the same temperature range by two different pairs of operators) in which a quantity of water of approximately the same heat capacity was substituted for the solution of hydrofluoric acid. The value used for the average heat capacity of water from 18° to 20° C. was that of Osborne, Stimson, and Ginnings (5), namely, 4.1817 int. j. per gm. per degree (0.9996 defined cal.). The value obtained for the "electrical energy equivalent" of the calorimeter was 44.6 j. (10.7 cal.) per degree.

As all the series of experiments with water and with the various concentrations of hydrofluoric acid were made under similar conditions, over the same range of temperature and with the same setting of the thermometer, errors peculiar to the apparatus tend to be eliminated in the final calculations of the specific heat of the acid.

A small error was probably introduced by the variation in the vapour tension of the acid solutions. It may be calculated that with pure water the heat required for the evaporation between 18° and 20° C. (into the 450 cc. of air saturated at 18° C. enclosed in the calorimetric system) is about 1 j. (0.25 cal.) per degree. This appears as a part of the "electrical energy equivalent" of the apparatus. With increasing concentration of acid the quantity of water evaporated during a determination of the heat capacity decreases slightly but this is partly offset by the evaporation of hydrogen fluoride. Vapour tension data for calculation of the error involved are not available. The error for the lower concentrations of acid is negligible, and, except perhaps with the highest concentrations of acid, is probably not greater than the mean precision error of the determinations.

The hydrofluoric acid was a commercial product of the highest quality (A. C. S. Specifications) and was used without further purification. The acid, which assayed 48.13% HF, gave negative tests for chloride and

TABLE I

HEAT CAPACITY DATA FOR AQUEOUS SOLUTIONS OF HYDROFLUORIC ACID*

Concentration of hydrofluoric acid				No. of determinations	Heat capacity C_p./gm./° C. (18° to 20° C.)			Apparent molal heat capacity of solute, cal.
%	Molality	Square root molality	Molal ratio H_2O/HF		International joules	Defined calories	$2\sqrt{\Sigma\Delta^2/n\ (n\text{-}1)}$, calories**	
48.13	46.37	6.81	1.20	3	3.005	0.7185	±0.0012	8.31
34.95	26.81	5.18	2.07	7	3.235	0.7734	±0.0010	7.04
25.10	16.75	4.09	3.31	5	3.470	0.8294	±0.0008	6.29
19.97	12.47	3.53	4.45	6	3.599	0.8603	±0.0004	6.05
14.96	8.791	2.96	6.31	4	3.730	0.8917	±0.0004	5.57
10.02	5.565	2.36	9.97	5	3.873	0.9258	±0.0004	5.28
5.26	2.775	1.67	20.00	7	4.014	0.9596	±0.0004	4.79
2.173	1.110	1.05	50.00	4	4.110	0.9824	±0.0001	4.15
1.459	0.740	0.86	75.00	3	4.134	0.9882	±0.0002	4.32
1.086	0.549	0.74	101.2	4	4.150	0.9919	±0.0005	5.8
0.551	0.277	0.53	200.3	4	4.165	0.9956	±0.0005	5.4

* *The weight of solution used in the calorimeter in the different series of experiments varied from 600 to 690 gm. with increasing concentration of acid. The temperature rise varied from 1.99° to 2.03° C., and the average final temperature varied from 20.02° to 20.10° C.*

** *This calculation of the "precision error" for each series of determinations gives a probability of 21 to 1 that the uncertainty of the mean experimental value does not exceed the limits indicated (8). $\Sigma\Delta^2$ is the sum of the squares of the individual deviations from the mean; n, the number of individual determinations in the series. Nine experiments with 600.64 gm. of distilled water in the calorimeter (heat capacity of water 18° to 20° C. = 600.64 × 4.1817 or 2511.7 int. j./° C.) gave an average total experimental heat capacity of 2556.1 int. j./° C. or a calculated "electrical energy equivalent" for the apparatus of 44.6 j. The value of $2\sqrt{\Sigma\Delta^2/n\ (n\text{-}1)}$ for the series is 0.6 j. The values given in this column may therefore be considered to be the calculated "21 : 1" final "precision error" for each series.*

sulphate, 0.002% non-volatile residue, and 0.03% fluosilicic acid (all tests according to A. C. S. Specifications for analytical reagents (1941)). Total acidity was determined by titration with carbonate-free sodium hydroxide, using a weight burette with phenolphthalein as indicator. Dilutions were made by weight and checked by titration after dilution. Paraffined glass vessels were used for handling the acid.

All weights were corrected to vacuum. The densities used in the calculations were obtained by interpolation from data given in International Critical Tables, and the atomic weights were the international values of 1941.

Experimental Results

Table I gives a summary of the significant data of the heat capacity determinations together with the calculated values for the apparent molal heat

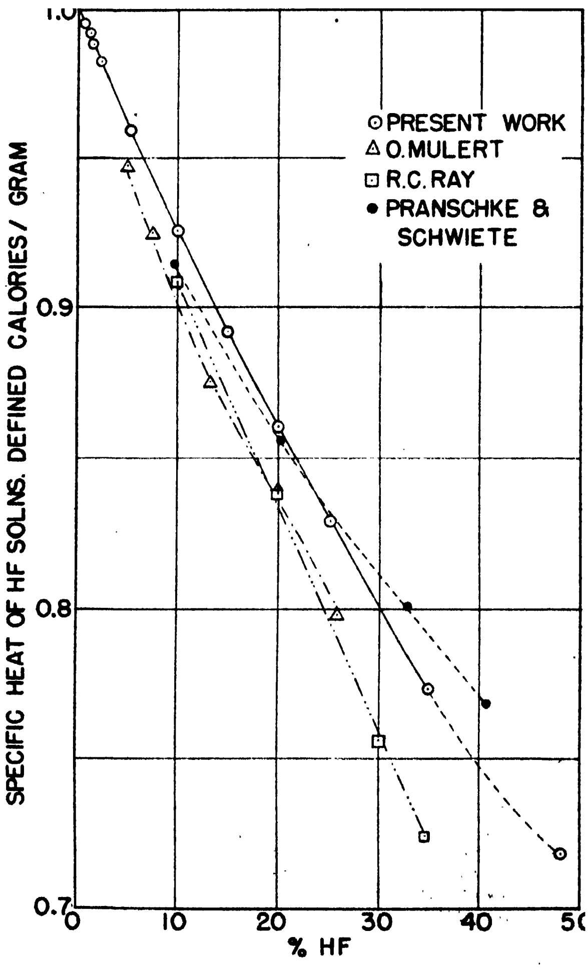

FIG. 1. *Specific heat of solutions of hydrofluoric acid in defined calories per gram.*

capacity of the solute. Fig. 1 gives graphically the specific heat data obtained in the present work and by previous investigators (4, 6, 7), and Fig. 2 the corresponding graphs for the apparent molal heat capacity of the solute plotted against the square root of the molality. In connection with the values for the apparent molal heat capacity of the solute in the two most dilute solutions, it should be noted that a change of less than 1 part in 1000 in the specific heat of the 1.086% solution and less than 1 in 3000 in the case of the 0.55% solution would bring the results into agreement with the other values on the graph.

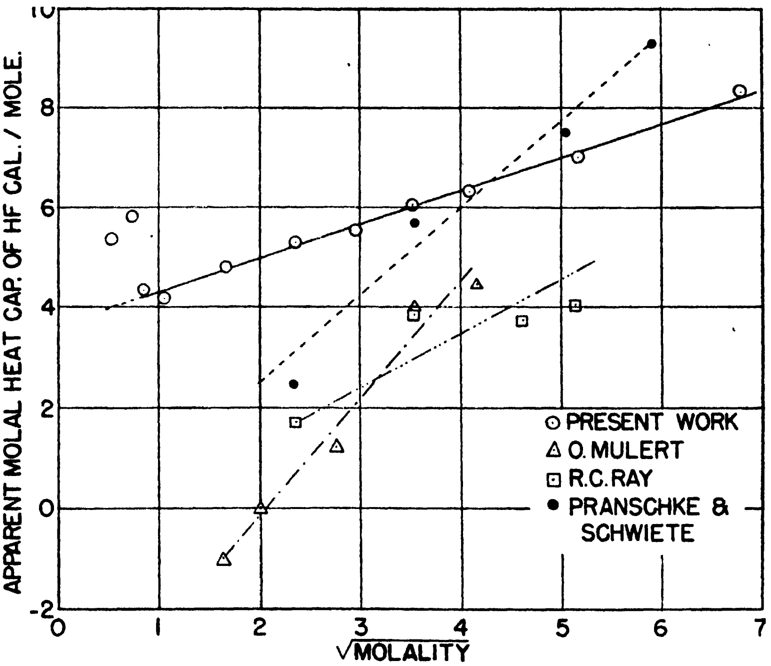

FIG. 2. *Apparent molal heat capacity of hydrogen fluoride (HF) in aqueous solutions of hydrofluoric acid.*

Discussion

In considering the plot of the apparent molal heat capacity of the solute against the root of the molality of the solution, it must be kept in mind that this gives a very sensitive method of comparing the consistency of the results. The curve for the data obtained in the present work shows that the results fall on a straight line except those for the two most dilute solutions. However, as already stated, the divergence represents less than 1 part in 1000 and 3000, respectively. It is also possible that these variations are significant, as Gucker and Schminke (2) obtained similar results with dilute solutions of hydrochloric acid.

The great variation between the results obtained by different experimenters as shown by these curves is rather disconcerting. It should, however, be stated that in most cases very few details of experimentation were reported. Mulert states that the measurements were usually made from 17° to 18° C., Pranschke and Schwiete state that the values are for 18 ± 1° C., while Ray does not give the temperature range of the measurements.

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THE ALKALOIDS OF *LYCOPODIUM* SPECIES

VII. *LYCOPODIUM LUCIDULUM* MICHX. (*UROSTACHYS LUCIDULUS* HERTER)[1]

BY RICHARD H. F. MANSKE[2] AND LÉO MARION[3]

Abstract

Nine alkaloids have been isolated from *Lycopodium lucidulum* Michx. Three of these, nicotine, lycopodine, and alkaloid L13, have been previously described. The remaining six are alkaloid L20 ($C_{17}H_{27}O_2N$), alkaloid L21 ($C_{18}H_{21}ON$), alkaloid L22 ($C_{16}H_{27}ON$), alkaloid L23 ($C_{16}H_{25}O_2N$), alkaloid L24 ($C_{16}H_{25}ON$), and alkaloid L25 ($C_{16}H_{25}O_2N$). These alkaloids represent but a small quantity of the total bases in the plant, the larger proportion of which it has not been possible to purify.

L. lucidulum Michx. is a more primitive plant than the other species of this genus that have been investigated. It exhibits the so-called "selago condition," a term used to indicate that the sporangia are borne in the axils of the leaves and not in a terminal spike as in most of the other Canadian species. Because of these and other characters *L. lucidulum* and related species have been relegated to a separate genus, namely, *Urostachys* Herter (5). Hutchinson and Wollack (1) have shown that the aluminium content of species of *Lycopodium* is much higher than that of species of *Urostachys* in Nessel's classification. With the single exception of *L. annotinum*, which is regarded as the most primitive of the genus, the aluminium content of the ash of lycopodiums may be as high as 20% and the aluminium in the dry plants often exceeds 0.1%. On the other hand, the aluminium in species of *Urostachys* seldom exceeds 0.1% and is occasionally less than 0.01%, amounts comparable to those normally present in other terrestrial plants. It was of interest, therefore, because of these characters of the plant to investigate the alkaloids it contains and ascertain what similarity might exist with those contained in the other species already studied.

A total of nine alkaloids have been isolated from *L. lucidulum*, three only of which, lycopodine, alkaloid L13, and nicotine, are common to other species. The ubiquitous lycopodine was found to be the major alkaloid and the second in importance is alkaloid L13, which is also present in *L. tristachyum* (3), *L. obscurum* (2), and *L. clavatum* (4). Nicotine was also isolated in small quantity.

The remaining alkaloids include alkaloid L20 ($C_{17}H_{27}O_2N$), alkaloid L21 ($C_{18}H_{21}ON$), alkaloid L22 ($C_{16}H_{27}ON$), alkaloid L23 ($C_{16}H_{25}O_2N$), alkaloid L24 ($C_{16}H_{25}ON$), and alkaloid L25 ($C_{16}H_{25}O_2N$). The quantities obtained of some of these alkaloids were very small considering the large quantity of

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plant used. Although the total quantity of ether-soluble bases amounted to 0.23%, the crystalline alkaloids isolated represent only about 0.05%. An even larger quantity of crude bases was soluble in chloroform but insoluble in ether. From this last quantity it has not yet been possible to isolate any homogeneous alkaloid.

Experimental

The plant material was collected in the neighbourhood of the Forestry Station at Duchesnay, north of Quebec City. Dried and ground it weighed 91.6 kgm. It was repeatedly extracted with cold methanol by percolation and the extract deprived of solvent by distillation in a steam-jacketed still. The thick syrup left after removal of the solvent was divided into a number of batches for convenience. The first batch was mixed with water, the mixture made acid to Congo with hydrochloric acid, heated on the steam-bath for 24 hr., and cooled. The voluminous insoluble material was filtered, heated again with dilute acid, and filtered cold. This second filtrate was added to the second batch, which was treated as the first. When the total extract had been thus treated the aqueous filtrates were basified with ammonia and exhaustively extracted with chloroform. The total base thus obtained was redissolved in dilute hydrochloric acid, the solution filtered through charcoal, extracted with ether (extract discarded), basified with ammonia, and repeatedly extracted with large portions of ether (Extract *A*). When ether failed to remove any more base, the extraction was continued with chloroform (Extract *B*).

Alkaloid L20

The combined ether extract *A* after evaporation yielded a thick gum (wt. 197 gm.), which partially crystallized on standing. This was stirred with an approximately equal volume of ether and the solution filtered to remove an insoluble crystalline residue, which was washed with ether and recrystallized repeatedly from boiling methanol from which it separated on cooling as colourless, elongated prisms; m.p. 259° C.*; wt. 1.0 gm. Found: C, 73.78, 73.78; H, 9.62, 9.56; N, 5.29, 5.26%. Calc. for $C_{17}H_{27}O_2N$: C, 73.65; H, 9.75; N, 5.05%.

Some of the above alkaloid was dissolved in methanol and the solution made just acid to Congo by the cautious addition of 65% perchloric acid. The crystalline perchlorate that separated on standing was recrystallized from methanol from which it separated as colourless prisms melting at 271° C. with previous discoloration. Found: C, 55.32, 55.11; H, 7.63, 7.48; N, 3.88, 3.81%. Calc. for $C_{17}H_{27}O_2N.HClO_4$: C, 54.04; H, 7.42; N, 3.71%.

The ether filtrate from base L20 was evaporated to dryness and the residue fractionated *in vacuo*. It yielded the following fractions: I, b.p. up to 150° C. (20 μ), wt. 46 gm.; II, b.p. 150° to 170° C. (25 μ), wt. 10.5 gm.; III, b.p. 170° to 180° C. (25 μ), wt. 4.5 gm. A very large gummy residue was left that could not be distilled at that pressure without decomposition.

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* *All melting points are corrected.*

Lycopodine

Fraction I was dissolved in acetone (70 cc.) containing methanol (2 cc.) and the solution made just acid to Congo with 65% perchloric acid. The crystalline perchlorate that separated was recrystallized once from boiling methanol and once from boiling water from which it separated in colourless prisms, m.p. 276° C. either alone or in admixture with a sample of lycopodine perchlorate. A quantity of this perchlorate was dissolved in hot water, the solution basified with ammonia, and the recovered base distilled *in vacuo* (b.p. 125° C. (20 μ)) and recrystallized from a little ether from which it was obtained as colourless prisms, m.p. 116° C. either alone or after admixture with lycopodine. The total weight of lycopodine obtained as perchlorate was 44.8 gm.

Alkaloid L13

The acetone mother-liquor from which the lycopodine perchlorate had separated was evaporated down to half its volume and the solution allowed to stand. A crop of crystals was deposited which was recrystallized from boiling methanol. This perchlorate melted at 274° C. and admixture with the perchlorate of alkaloid L13 failed to depress the melting point; wt. 20 gm. A quantity of this salt (5 gm.) was dissolved in boiling water, the solution basified with ammonia, and the recovered base crystallized twice from absolute ether. The base consisted of colourless flat prisms, m.p. 129° C., and in admixture with the base L13 (m.p. 130° C.) it melted at 130° C.

The acetone mother-liquor was diluted with water and heated on the steam-bath until the organic solvents were removed. The hot solution was then basified with ammonia, the mixture cooled, and extracted repeatedly with ether. The combined ether extract was distilled to dryness and the residue refractionated *in vacuo:* fraction *a*, b.p. 75° to 80° C. (0.3 mm.), wt. 0.14 gm.; fraction *b*, b.p. 85° to 90° C. (0.3 mm.), wt. 2.35 gm.; fraction *c*, b.p. 110° to 135° C. (0.3 mm.), wt. 5.79 gm.; fraction *d*, b.p. 150° to 180° C. (0.3 mm.), wt. 4.81 gm.; and fraction *e*, b.p. 180° to 200° C. (0.6 mm.), wt. 1.03 gm.

Nicotine

Fraction *a* obtained above consisted of a colourless oil which was dissolved in methanol and added to a methanolic solution of picric acid. A lemon-yellow picrate immediately separated, m.p. 226° C. either alone or after admixture with an authentic sample of nicotine dipicrate.

Alkaloid L21

Fraction *b* consisted of a slightly yellowish oil. It was dissolved in a little methanol and the solution cautiously neutralized with 65% perchloric acid. An equal volume of absolute ether was added to the solution, which was kept several hours in the refrigerator. The perchlorate which had crystallized was filtered, washed with a mixture of methanol and absolute ether, and recrystallized from the same mixture from which it formed aggregates of flat needles, m.p. 201° C. Found: C, 50.25, 50.28; H, 7.33, 7.29; N, 4.29, 4.33%. Calc. for $C_{13}H_{21}ON.HClO_4.0.5CH_4O$: C, 50.07; H, 7.42; N, 4.33%.

Some of the perchlorate was reconverted to the base, which was dissolved in methanol and added to a methanolic solution of picric acid. The solution was concentrated and allowed to stand. After several days a picrate separated, which, after one crystallization from methanol, consisted of long, soft, lemon-yellow needles, m.p. 107° C. Found: C, 52.64, 52.32; H, 6.07, 5.52; N, 12.98, 13.02%. Calc. for $C_{13}H_{21}ON.C_6H_3O_7N_3$: C, 52.29; H, 5.51; N, 12.84%.

Fraction *c* was dissolved in methanol and the solution neutralized with 65% perchloric acid. A perchlorate crystallized out which proved to be that of lycopodine. The filtrate was diluted with water and heated on the steam-bath to remove the methanol. After several days at room temperature the aqueous solution deposited a quantity of crystals, which, after recrystallization from methanol–ether, melted at 201° C. and were identical with the perchlorate of alkaloid L21.

Alkaloid L22

Fraction *d*, b.p. 150° to 180° C. (0.3 mm.), was dissolved in methanol and neutralized with 65% perchloric acid. After a few days at room temperature the solution had deposited a perchlorate, which was filtered and recrystallized from boiling methanol (charcoal) from which it separated as small, colourless prisms, m.p. 254° C. with previous sintering. Wt. 1.5 gm. Found: C, 54.20, 54.83; H, 7.79, 7.88; N, 4.13, 4.03%. Calc. for $C_{16}H_{27}ON.HClO_4$: C, 54.94; H, 8.01; N, 4.00%.

Some of the above perchlorate was dissolved in hot water and the solution basified with ammonia. After cooling, the precipitated base was extracted with ether. The base recovered from the ether was a colourless oil that crystallized on standing. It was recrystallized twice from petroleum ether by cooling in dry-ice–acetone. The base, obtained as colourless crystals, begins to sinter at 101° C. and melts at 108° C. Found: C, 76.93; H, 10.30; N, 5.73%. Calc. for $C_{16}H_{27}ON$: C, 77.11; H, 10.84; N, 5.62%.

Alkaloid L23

The combined mother-liquors from the recrystallizations of the perchlorate of L22 were evaporated down to a small volume and allowed to stand. A crystalline perchlorate was deposited which after several recrystallizations from a boiling mixture of methanol and ethyl acetate was obtained as colourless prisms, m.p. 300° C., wt. 0.9 gm. Found: C, 53.24, 53.07; H, 7.02, 7.31; N, 3.85, 3.86%. Calc. for $C_{16}H_{25}O_2N.HClO_4$: C, 52.82; H, 7.15; N, 3.85%.

A small quantity of this perchlorate was dissolved in hot water and the solution basified with ammonia. The base was extracted with ether from the cooled solution and, after removal of the solvent, distilled *in vacuo*. It sublimed at 130° to 145° C. (0.2 mm.) as colourless prisms, m.p. 161° to 162° C. Recrystallization from petroleum ether did not alter the melting point. Found: C, 73.82; H, 9.99; N, 5.62, 5.41%. Calc. for $C_{16}H_{25}O_2N$: C, 73.00; H, 9.50; N, 5.32%.

Alkaloid L24

The mother-liquor from the crystallization of L23 perchlorate was diluted with water and the solution heated on the steam-bath until the organic solvent had evaporated. This solution, on cooling, deposited a mixture of crystals and gum, which was filtered and dissolved in hot methanol. The methanolic solution after some time deposited a crystalline perchlorate, which, when recrystallized twice more from methanol, was obtained as large, colourless feathery aggregates, m.p. 278° C., wt. 0.38 gm. Found: C, 55.86, 55.87; H, 8.14, 8.05; N, 4.09, 4.16%. Calc. for $C_{16}H_{25}ON.HClO_4$: C, 55.25; H, 7.48; N, 4.03%. Admixture with lycopodine perchlorate depressed the melting point to 274° C.

Alkaloid L25

Fraction *e*, b.p. 180° to 200° C. (0.6 mm.) was dissolved in methanol, and the solution neutralized with 65% perchloric acid and kept in the refrigerator for several days. The perchlorate which had crystallized was filtered and recrystallized from boiling methanol from which it separated in short colourless needles, m.p. 297° C., wt. 0.3 gm. When mixed with the perchlorate of alkaloid L23, it melted at 260° to 265° C. Found: C, 52.47, 52.19; H, 7.38, 7.43; N, 3.69, 3.53%. Calc. for $C_{16}H_{25}O_2N.HClO_4.0.5\ H_2O$: C, 52.18; H, 7.38; N, 3.69%.

The mother-liquor of this perchlorate yielded a further small quantity of alkaloid L23.

Fraction II from the original fractionation, b.p. 150° to 170° C. (25 μ), crystallized on standing. It was shaken with ether (30 cc.) until no more of the crystalline mass would dissolve. The mixture was filtered and the insoluble base recrystallized from methanol. It melted at 259° C. and was found to be identical with alkaloid L20. The ether filtrate was evaporated to dryness, the residue dissolved in acetone and the solution neutralized with 65% perchloric acid. After cooling in the refrigerator, a copious precipitate of a crystalline perchlorate had formed which was found to be identical with lycopodine perchlorate. The mother-liquor from the foregoing perchlorate was diluted with water and heated on the steam-bath until the methanol had evaporated. The solution was basified with ammonia and extracted with ether. The basic material obtained from the extract was fractionated *in vacuo*. It yielded several fractions from which further small quantities of nicotine and alkaloids L21 and L24 were isolated.

Fraction III, b.p. 170° to 180° C. (25 μ) consisted of a dark gum, which was shaken with ether and the solution filtered to remove some insoluble, amorphous material. The filtrate was evaporated to dryness, the residue dissolved in methanol, the solution neutralized with 65% perchloric acid and cooled in the refrigerator. The perchlorate which crystallized out was filtered and washed with methanol. It was identical with lycopodine perchlorate. The mother-liquor was concentrated on the steam-bath and again cooled in the refrigerator for several days in the course of which a second perchlorate crystallized out. This was recrystallized from boiling methanol (charcoal) from which it separated as colourless prisms, m.p. 265° C. alone or in admixture with the perchlorate of alkaloid L20.

The chloroform extract *B* was dissolved in hot dilute hydrochloric acid, and the solution cooled, filtered through charcoal, and thoroughly extracted with ether. It was basified with ammonia and extracted with 15 large portions of ether and then with chloroform.

The ether extract was evaporated until the solution had reached a concentration of about 50%. On cooling, this deposited a further quantity of alkaloid L20. The ether filtrate was evaporated to dryness, and the basic residue dissolved in methanol and neutralized with 65% perchloric acid. This when worked up exactly as described for the main portion of the ether-soluble bases yielded further small quantities of the alkaloid perchlorates already mentioned.

In all cases the yield of alkaloid given is the total weight of that alkaloid or its perchlorate found in the plant. The weight of the ether-soluble alkaloids that could not be distilled below 200° C. at the pressures used is greater than that of the total alkaloids isolated either as crystalline bases or as their perchlorates. It has not yet been possible to induce crystallization of this relatively large quantity of amorphous base.

The quantity of ether-insoluble base which was extracted with chloroform is also very large and no success has so far been achieved in obtaining any tractable substance from it.

Acknowledgment

The plant material used in this investigation was placed at our disposal by Prof. P. L'Ecuyer of Laval University, Quebec, to whom we express our best thanks.

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THE ALKALOIDS OF *LYCOPODIUM* SPECIES

VIII. *LYCOPODIUM SABINAEFOLIUM* WILLD.[1]

By Léo Marion[2] and R. H. F. Manske[3]

Abstract

A total of four alkaloids have been isolated from *Lycopodium sabinaefolium* Willd. Three of these have already been found to occur together in other species, while the fourth, alkaloid L26 ($C_{15}H_{25}ON$), appears to be new.

In continuation of a series of researches on the alkaloids of *Lycopodium* species, an investigation of *Lycopodium sabinaefolium* Willd. is now reported. This plant, which does not appear to be as plentiful as some of the species already studied, contains four alkaloids. Three of these, i.e., lycopodine, alkaloid L13, and nicotine have already been found to occur together in *L. tristachyum* (3), *L. clavatum* (4), and *L. lucidulum* (2). The fourth, alkaloid L26 ($C_{15}H_{25}ON$), has not been found in the other species investigated so far. It is noteworthy that alkaloid L26 is the first C_{15}-alkaloid isolated in the *Lycopodium* series. Lycopodine is the main alkaloid occurring in this plant, while alkaloid L13 is obtained in a yield about half that of the former.

The plant material was identified by Mr. C. A. Weatherby of the Gray Herbarium, Harvard University, and by Dr. H. A. Senn of the Division of Botany and Plant Pathology, Central Experimental Farm, Ottawa, who were consulted independently, and the opportunity is taken to express grateful thanks.

Experimental

L. sabinaefolium Willd. was collected in late summer in the neighbourhood of Lake Timiscaming, in northern Quebec, by Mr. J. N. Chabot of the Department of Agriculture of the Province of Quebec to whom the authors acknowledge their indebtedness. The dried and ground plant weighed 1600 gm. It was extracted in Soxhlets with methanol and the solvent largely distilled from the combined extract. The residue was diluted with water and made acid to Congo by the addition of a slight excess of hydrochloric acid. The mixture was heated for 16 hr. on the steam-bath, cooled to room temperature, and subsequently in the refrigerator. It was filtered and the insoluble matter heated again with dilute hydrochloric acid and treated similarly. The combined filtrate was basified with ammonia and exhaustively extracted with chloroform.

The base obtained on evaporation of the chloroform was redissolved in warm, dilute hydrochloric acid and the solution filtered with suction through a layer of charcoal. The filtrate was thoroughly extracted with ether, made definitely basic with ammonia, and extracted first with five portions of ether and then with five portions of chloroform. From the combined ether extract a thick residual oil was obtained, wt. 2.2 gm., while the chloroform extract yielded a dark gum, wt. 1.0 gm. The combined weight of crude base represents a yield of 0.2%.

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[1] *Manuscript received November 24, 1945.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1355.

[2] *Chemist.*

[3] *Director, the Research Laboratory, Dominion Rubber Co. Ltd., Guelph, Ont.*

The dry ether-soluble base (2.2 gm.) when fractionated *in vacuo*, yielded the following fractions: I, a slightly yellowish oil, b.p. 135° to 140° C. (0.35 mm.), wt. 1.96 gm.; II, yellowish oil, b.p. 141°-145° C. (0.35 mm.), wt. 0.216 gm.; and a small undistilled residue. Both fractions I and II crystallized on cooling.

Lycopodine

The crystalline base obtained as fraction I was dissolved in boiling dry ether and the solution allowed to stand. It deposited beautiful colourless prisms, m.p. 116° C.* either alone or in admixture with an authentic specimen of lycopodine. The mother-liquor was evaporated to dryness and the residual oil dissolved in acetone. This solution was made just acid to Congo with 65% perchloric acid. After an hour the crystalline perchlorate which had started to separate almost immediately was filtered and washed with methanol. It melted at 283° C. and admixture with lycopodine perchlorate failed to depress the melting point. The total weight of base obtained as such or as perchlorate was 1.73 gm.

Alkaloid L13

The acetone solution from which lycopodine perchlorate had crystallized, when concentrated to half its volume and cooled, deposited a further small quantity of lycopodine perchlorate. The final mother-liquor was diluted with water and the solution heated on the steam-bath until the organic solvent had evaporated. After cooling, this solution deposited a crystalline perchlorate, which was filtered and recrystallized from boiling methanol. It separated in aggregates of colourless small rhombs, melting at 274° C. either alone or in admixture with the perchlorate of alkaloid L13. The total weight of this base obtained was 0.49 gm. Some of this perchlorate was dissolved in hot water, the solution basified with ammonia, and the precipitated base extracted with ether. The base recovered from the extract was recrystallized from ether and obtained as colourless prisms, m.p. 130° C. Admixture with alkaloid L13 failed to depress the melting point.

Fraction II, b.p. 141° to 145° C. (0.35 mm.) was dissolved in methanol and the solution made just acid to Congo with 65% perchloric acid. On standing, small colourless prisms were deposited, m.p. 275° C. Admixture with the perchlorate of alkaloid L13 failed to depress the melting point. Water was added to the mother-liquor, which was heated on the steam-bath until the methanol had evaporated. This aqueous solution was combined with the final aqueous mother-liquor from the alkaloids of fraction I, basified with ammonia, and exhaustively extracted with ether. The combined ether extract was distilled to dryness and the residual oil refractionated *in vacuo*. A very small first fraction was obtained as a colourless oil, b.p. 85° to 95° C. (0.6 mm.) and the bulk as a thick oil, b.p. 135° to 145° C. (0.6 mm.), which crystallized on standing.

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* *All melting points are corrected.*

Nicotine

The small fraction of oil (b.p. 85° to 95° C. (0.6 mm.)) obtained was dissolved in methanol (1 cc.) and added to a solution of picric acid in methanol (1 cc.). The resulting solution was evaporated to about half its volume and allowed to stand. It deposited a picrate as lemon-yellow prismatic needles, which, when dried, weighed less than 1 mgm. Mixed with an approximately equal quantity of an authentic specimen of nicotine dipicrate it failed to depress the melting point of the latter (226° C.).

Alkaloid L26

The refractionated base, b.p. 135° to 145° C. (0.6 mm.), was dissolved in dry ether, and the solution concentrated to a small volume and cooled in the refrigerator. It deposited a base in the form of small, stout, colourless prisms, which, after one recrystallization, melted at 171° C. In admixture with alkaloid L11 (m.p. 174° C.) (1), it began to sinter at 150° C. and was completely liquid at 158° C. Wt. 20 mgm. Found: C, 76.85; H, 10.61; N, 6.02%. Calc. for $C_{15}H_{25}ON$: C, 76.60; H, 10.64; N, 5.96%.

The base obtained from the original chloroform extract was fractionated *in vacuo* into two fractions, which were converted to perchlorates in methanol. Both yielded further quantities of the perchlorate of alkaloid L13.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XL. *CORYDALIS CORNUTA* ROYLE[1]

By Richard H. F. Manske[2]

Abstract

Only protopine and *d*-stylopine have been isolated in amount sufficient for identification from *Corydalis cornuta*. Though closely related taxonomically to *C. sibirica* and *C. ochotensis* only the presence of acetyl-ornithine confirms this similarity. It is suggested that *C. ochotensis* is a polyploid form of *C. cornuta*.

For convenience in taxonomy the genus *Corydalis* has been subdivided into a number of sections and subsections. *Corydalis cornuta* Royle has been placed in the section Eucorydalis Prantl, subsection Ramoso-sibiricae Fedde along with *C. sibirica* (2) and *C. ochotensis* (4) whose chemical examination has already been recorded. There is ample morphological evidence to justify such a relationship. On casual examination *C. cornuta* appears to be a smaller form of *C. ochotensis* and like the latter it is an obligate biennial.

The three plants are the only ones known to elaborate acetyl-ornithine, an observation that lends support to the taxonomic evidence of similarity. It was therefore anticipated that at least some of the alkaloids found in *C. sibirica* or *C. ochotensis* would also be found in *C. cornuta*. Nevertheless, only the ubiquitous protopine was found in the three plants. Indeed, *C. cornuta* is unique in the genus *Corydalis*. It contains only a very small amount of total alkaloids and this consists largely of protopine. The only other alkaloid that could be isolated in amounts sufficient for identification was *d*-stylopine, which does not occur in the other two species mentioned. Minute quantities of two other bases were isolated, but neither was identical with bases already isolated from either *C. sibirica* or *C. ochotensis*.

It is obvious that, in view of the presence of acetyl-ornithine in this plant, it cannot be separated from the subsection Ramoso-sibiricae. It is equally obvious that the absence of characteristic alkaloids does not admit of such a classification unless a satisfactory explanation can be found. No such explanation is yet at hand but the writer ventures to suggest that *C. ochotensis* is a polyploid form of *C. cornuta*, and that for reasons not yet known the several forms are stable and persistent.

The writer is indebted to Dr. R. R. Stewart, Gordon College, Rawalpindi, India, who collected some plant material and supplied a quantity of seed from which the major portion of the material was grown. (The collection was made at an altitude of 7000 ft. on Naini Tal, Kumaon, U.P. India.) It is pertinent to note that the plant was grown in the same garden in which *C. sibirica* and *C. ochotensis* for previous investigations had been grown.

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[1] *Manuscript received November 5, 1945.*
Contribution from the Research Laboratory, Dominion Rubber Company Limited, Guelph, Ont.

[2] *Director of Research.*

Experimental

There was available 400 gm. of the dried one-year-old roots and 11.3 kgm. of dried aerial portion. The acetyl-ornithine was isolated as described (3). A total of 6 gm. of purified amino acid was obtained.

The mother-liquors from the acetyl-ornithine were combined with the extract from the aerial portion and the whole worked up by the author's standardized procedure (1).

Protopine

The fraction BS yielded no other bases than protopine. It was recrystallized from chloroform–methanol until it melted alone or in admixture with an authentic specimen at 211° C.* The yield was about 0.03%.

d-Stylopine

The fraction BC was redissolved in hot dilute hydrochloric acid and the filtered solution set aside. The colourless crystals of hydrochloride that separated were converted to free base and the latter recrystallized from hot methanol. The colourless needles thus obtained melted at 202° C. In admixture with *l*-stylopine it melted indefinitely at 206° to 220° C. It was obvious therefore that the base was *d*-stylopine and this was confirmed by recrystallizing equal amounts of this base and *l*-stylopine from chloroform–methanol. The brilliant colourless prisms thus obtained melted either alone or in admixture with authentic *dl*-stylopine at 223° C. The yield was about 0.02%.

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* *All melting points are corrected.*

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SYNTHESIS OF SOME ANALOGUES OF 1,1-BIS-(*p*-CHLOROPHENYL)-2,2,2-TRICHLOROETHANE (DDT)

I. THREE FLUORINE ANALOGUES[1]

BY S. KIRKWOOD[2] AND J. R. DACEY[3]

Abstract

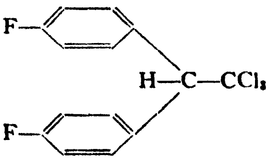
The compounds 1,1-bis-(*p*-fluorophenyl)-2,2,2-trichloroethane, 1,1-bis-(*p*-chlorophenyl)-2,2,2-trifluoroethane, and 1,1-bis-(*p*-fluorophenyl)-2,2,2-trifluoroethane have been prepared, and their method of preparation is outlined. The toxicity of these compounds to *Drosophila melanogaster* supports Läuger's hypothesis of the mechanism of the action of DDT.

Introduction

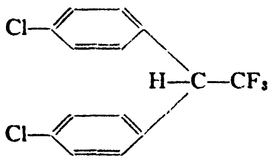
The great efficiency of the compound 1,1-bis-(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) as an insecticide makes it desirable to synthesize analogous molecules and determine their potency as insecticides. In this manner some knowledge may be obtained of the structural features of the DDT molecule responsible for its great toxicity; further, any useful and interesting tendencies towards a species specificity in any of the analogous molecules may be noted.

Experimental

The following compounds were prepared as outlined below.



I



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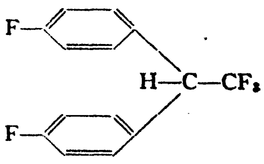

III

1,1-Bis-(p-fluorophenyl)-2,2,2-trichloroethane (I)

This compound was prepared by carrying out the Baeyer condensation using chloral and fluorobenzene (5). Fluorobenzene is conveniently prepared using Flood's adaptation of the Schiemann reaction (1).

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[1] *Manuscript received November 14, 1945.*

Contribution from the Chemical Warfare Laboratories, Department of National Defence (Army), Ottawa, Canada.

[2] *Lieutenant, Canadian Army.*

[3] *Major, Canadian Army.*

Chloral hydrate (69.5 gm., 0.42 moles) was dissolved in 400 ml. of concentrated sulphuric acid contained in a three-necked flask. While the solution was kept under vigorous agitation with a propellor type stirrer, 80 gm. (0.84 moles) of fluorobenzene was added and the temperature controlled at 45° C. Sixty millilitres of 20% fuming sulphuric acid was added during the course of the reaction. After two hours the acid mixture was poured over ice and the fluoro compound extracted with ether. The ether was washed twice with water and dried with sodium sulphate. After removal of the ether the compound was distilled under reduced pressure.

The product was a colourless viscous liquid that crystallized on standing and had a characteristic odour. Yield, 90 gm. (67%); b.p., 153° C. (at approx. 6 mm.); m.p., 41° to 42° C. corr. Calc. for $C_{14}H_9Cl_3F_2$: Cl, 33.2; F, 11.82%. Found: Cl, 33.97, 34.41; F, 11.91, 11.77%.

1,1-Bis-(p-chlorophenyl)-2,2,2-trifluoroethane (II)

This compound was prepared by the fluorination of DDT using Henne's method (3).

DDT (40 gm., 0.11 moles) was placed in a large platinum dish and thoroughly mixed with 54.4 gm. (0.25 moles) of mercuric oxide. The dish was placed in a good hood and an excess of liquid hydrogen fluoride was added. The mixture was stirred and the dish set aside until the excess hydrogen fluoride had evaporated. It was then poured over ice, and the water suspension filtered through a layer of filtercel on a Büchner funnel. The material on the funnel was thoroughly washed with water and then the organic materials were washed through with boiling ethanol. On diluting the ethanol with water a low melting crystalline solid separated out. Twenty-seven grams of material was obtained which melted over the range 45° to 50° C. and which was apparently a mixture of mono-, di-, and trifluoro DDT.

These fluoro compounds were quite difficult to separate by recrystallization, their solubilities being apparently very similar. Methyl alcohol was found to be the best solvent; the material was therefore recrystallized from it by dry-ice–acetone cooling. Five such recrystallizations resulted in a yield of 8.5 gm. of a white nicely crystalline compound with a characteristic odour. The melting point was sharp and could not be raised by further recrystallization; m.p., 64° to 65° C. corr. Calc. for $C_{14}H_9Cl_2F_3$: Cl, 23.3; F, 18.69%. Found: Cl, 22.94, 23.19; F, 18.52, 18.71%.

1,1-Bis-(p-fluorophenyl)-2,2,2-trifluoroethane (III)

This compound was prepared by the fluorination of 1,1-bis-(*p*-fluorophenyl)-2,2,2-trichloroethane (I). Thirty grams (0.94 moles) of (I) was placed in a platinum dish and thoroughly mixed with 46·8 gm. (0.22 moles) of mercuric oxide. The mixture was treated with hydrogen fluoride and worked up in the same manner as Compound (II). The product was a mixture of 17 gm. of white crystalline fluorides, which melted over the range 70° to 80° C. Repeated recrystallization from methanol using dry-ice–acetone cooling brought it up to a constant melting point. The result was a white nicely crystalline compound with a characteristic odour; m.p., 79° to 80° C. Calc. for $C_{14}H_9F_5$: Cl, 0.00; F, 34.92%. Found: Cl, 0.87, 0.75; F, 34.75, 34.88%.

It was desirable to know with certainty the extent to which fluorination had taken place in Compounds (II) and (III), there being no guarantee that all three chlorines on carbon atom No. 2 of the ethane nucleus could be replaced by Henne's technique. Since carbon and hydrogen determinations in organic compounds containing fluorine are often unreliable, it was decided that a direct determination of both chlorine and fluorine would give a more accurate measure of the extent to which fluorination had occurred. The chlorine analysis by the Carius method was quite satisfactory, the high solubility of silver fluoride preventing it from interfering. The method of McCombie and Saunders* was used to determine the fluorine content. The results using this method were quite satisfactory and establish the extent of fluorination beyond doubt.

These compounds were submitted to the Department of Genetics of McGill University for an assay of their potency as insecticides. The test insect was *Drosophila melanogaster*. The results were as follows:

Compound	Potency
I	2/5 that of pure DDT
II	1/100 that of pure DDT
III	1/100 that of pure DDT

Discussion

Läuger *et al.* (4) have given a summary of the investigations carried out by the J. R. Geigy Company that led to the discovery of the insecticidal powers of the DDT molecule. He postulates that the extreme toxicity of DDT is due to the basic toxicity of the *p*-bridged 4,4′-dichlorodiphenyl structure, coupled with the augmenting effect of the chloroform residue. The *p*-bridged 4,4′-dichlorodiphenyl structure probably acts by an enzyme-blocking mechanism while the chloroform residue, he claims, acts as a lipophilic group, which causes the molecule to have an affinity for the nerve lipoids. In order to test this hypothesis a number of molecules were synthesized which possessed the same 1,1-(*p*-chlorophenyl)ethane structure as DDT but which had residues corresponding to inhalation anaesthetics other than chloroform. All the molecules possessed insecticidal activity and their activity varied roughly as the partition coefficient of the anaesthetic whose residue was used to replace that of chloroform. Thus there seems to be some justification for Läuger's hypothesis of the mechanism of the action of DDT.

In order to carry these studies further, the above compounds were synthesized. On the basis of Läuger's hypothesis, (II) and (III) at least should be inactive, since fluoroform has no anaesthetic or other physiological effects when inhaled (2).

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* *Private communication.*

As would be expected from Läuger's hypothesis, (II) and (III) have little or no activity. What activity they do possess may well be due to slight contamination by the parent compounds from which they were made, i.e., DDT and (I). Since both of these compounds are extremely active, even traces would show activity at 100 times the concentration of pure DDT.

Acknowledgment

Acknowledgment is made to McGill University for assistance in having the biological assay made, and to Dr. Léo Marion of the National Research Council, whose laboratory carried out the micro-Carius determinations.

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FLOW-PRESSURE RELATIONS IN CALCIUM-SOAP-OIL SYSTEMS[1]

WILFRED GALLAY[2] AND IRA E. PUDDINGTON[3]

Abstract

Flow-pressure relations have been determined for suspensions of calcium soaps in mineral oils of varying viscosity and viscosity index. The effect of small amounts of reagents on the character of these curves is very marked. The addition of water generally increases the yield value of the system without affecting the mobility, while solvents for calcium soaps tend to change the mobility without altering the yield value.

Introduction

Flow-pressure curves in two-phase systems rarely follow the predictions of Poiseuille's equation and they usually show some type of anomalous flow. It is to be expected that the flow properties of lyophobic suspensions will be influenced by any interaction between the solid particles as well as by the volume they occupy. If the particles are completely independent of one another and are of such a shape that close packing may be obtained, dilatancy will probably result. If, however, the solid particles attract one another and form aggregates, a definite amount of pressure may have to be applied to cause flow. In such cases yield values will be found.

Since it has been shown (3, 4) that small amounts of addition agents sometimes have a large effect on the degree of flocculation of certain dispersions in organic media, viscometric measurements on these systems become of interest. The present communication deals with the results obtained when the viscosities of calcium-soap-mineral-oil dispersions were measured. Systems of this type form one of the larger groups of lubricants in use to-day, viz., the calcium base lubricating greases, and a knowledge of their flow properties becomes of obvious commercial interest.

Experimental

A laboratory-made viscometer of the Stormer type, shown diagrammatically in Fig. 1, with a rotating paddle and a stator fitted with baffles, was used in this work. The stator, although rigidly clamped in place during a determination, could be rotated by means of a motor to provide mechanical stirring of the mix. An air thermostat about the rotor and stator gave adequate temperature control. Flow-pressure curves were obtained by plotting the rate of fall of the basket against the load in the basket. The true viscosity of the system is then represented by the slope of the curve, and the yield value

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[1] *Manuscript received November 5, 1945.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1380.

[2] *Formerly, Chemist, National Research Laboratories; now, Consulting Chemist, Ottawa, Canada.*

[3] *Chemist.*

by the intercept on the pressure axis. Experiment showed that a load of 3 gm. was required to turn the rotor with the stator empty, and this value should be used as a blank in examining the graphs.

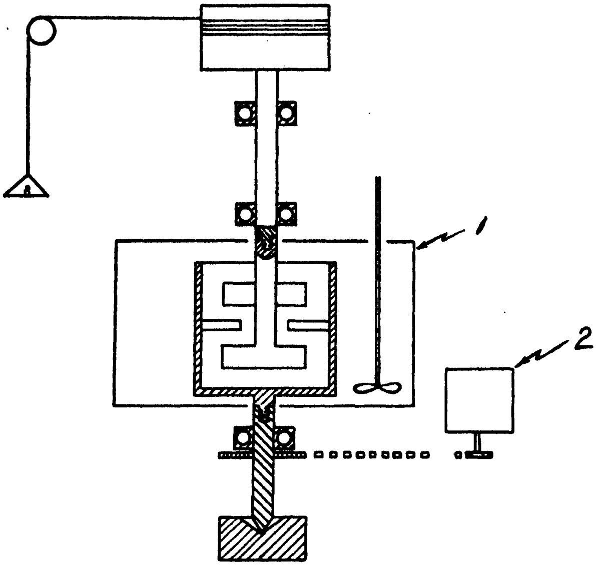

FIG. 1. *Diagram of viscometer: 1, air thermostat; 2, stirring motor.*

Fig. 2 shows the results obtained with this instrument using three mineral oils of different viscosities. Curves 1, 2, and 3 represent flow-pressure relations for oils having viscosities of 5000, 2000 and 300 Saybolt Universal Seconds at 100° F.

Viscosities were determined on suspensions of calcium soaps, with and without addition agents, in mineral oils that varied both in viscosity and viscosity index. Most of the measurements were made at room temperature since it was found that the results obtained here were substantially the same as those found at higher temperatures. Some of the more noteworthy results are shown graphically in the next section.

Results

Calcium Stearate

The results reported here were obtained with City Chemical Company pure calcium stearate.

In order to determine the effect of stirring on the flow properties of calcium-stearate-oil dispersions, measurements were made at various time intervals after the dispersions were made up. Fig. 3 shows the results obtained with a 40% suspension of calcium stearate in an oil with a viscosity of 150 S.U.S. at 100° F. and a viscosity index of 70. The points for Curves 1, 2, 3, 4, 5, and 6 were found after 0, 10, 20, 30, 90, and 190 min. of stirring, respectively. Curve 7 shows the effect of adding 1.5% of a soap solvent (citral) and Curve 8 gives the result when 5% of water, based on the soap, is added. It is immediately seen that the soap solvent has virtually no effect on the flow properties of the dispersion, while water changed the yield value markedly without altering the mobility of the material.

Changes in the flow properties with increasing dispersion are sufficiently small after 30 min. of stirring to have little effect on subsequent measure-

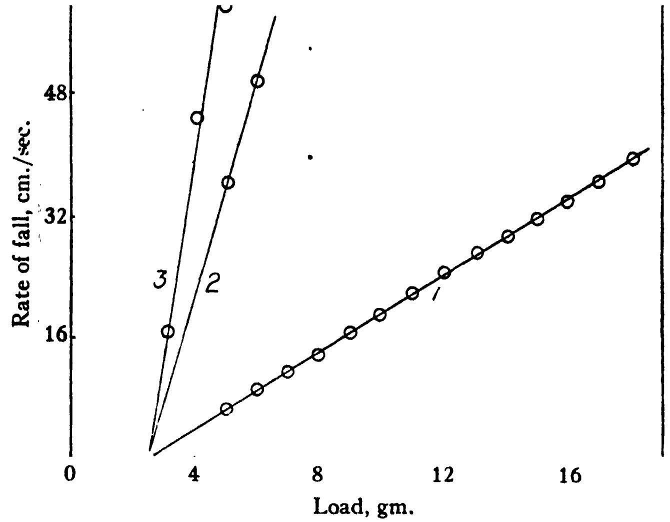

FIG. 2. *Flow-pressure curves for liquids: 1, 2, and 3 represent results obtained with mineral oils with viscosities of 5000, 2000, and 300 S.U.S. at 100° F., respectively.*

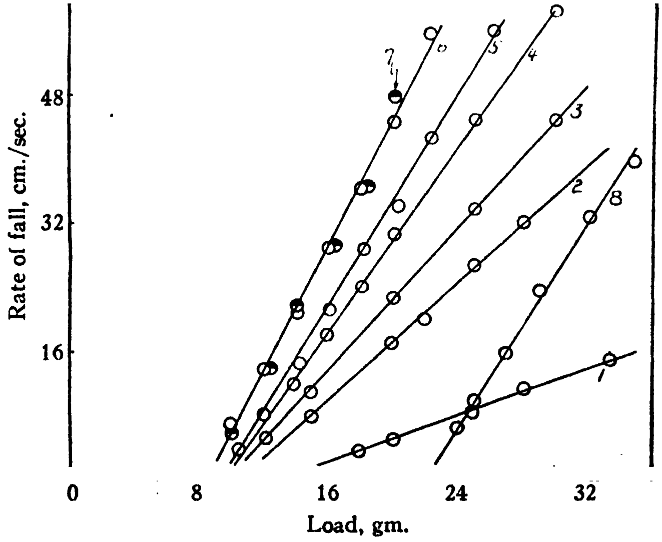

FIG. 3. *Flow-pressure curves for calcium-stearate-oil suspensions: 1, 2, 3, 4, 5, and 6 taken after 0, 10, 20, 30, 90, and 190 min. of stirring; 7, after the addition of 1.5% of citral; 8, after addition of 5% of water.*

ments, and the procedure of stirring each new sample for 30 min. and an additional 10 min. for each portion of addition agent added, before measurements were taken, was adopted.

The effect of increasing amounts of water is shown in Fig. 4, where Curves 1, 2, 3, and 4 represent the result of additions of 0.0, 1.1, 2.7, and 6.7% of water (based on the soap) to a suspension of 30% of calcium stearate in a mineral oil with a viscosity of 150 S.U.S. at 100° F. and a viscosity index of 70.

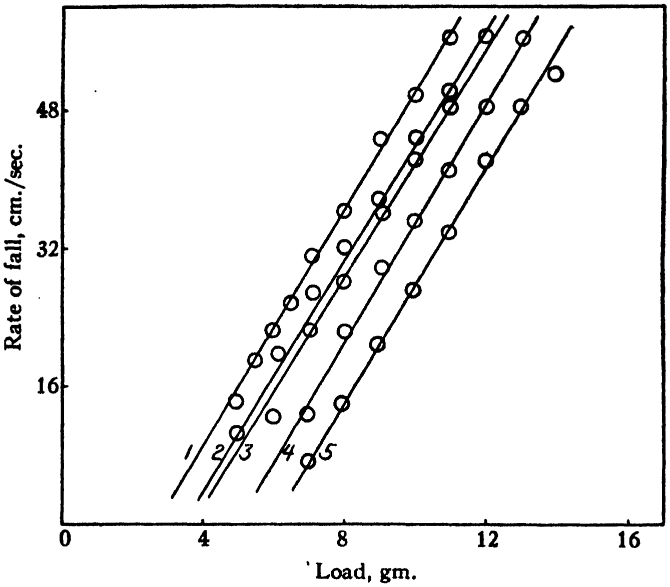

FIG. 4. *Flow-pressure curves for calcium-stearate-oil suspensions: 1, 2, 3, and 4 taken after addition of 0.0, 1.1, 2.7, and 6.7% of water; 5, same composition as 4, taken after standing overnight.*

Further additions of water up to 13.4% did not change the flow properties. After standing overnight the yield value increased as shown by Curve 5. Here again the addition of water has changed the yield value only.

Additions of glycerol to these systems produce results similar to those yielded by water but the effect is considerably less. The effect of free stearic acid is intermediate between that of water and glycerol.

Fig. 5 shows the effect of changing the concentration of soap while the soap-to-water ratio remains constant. Curves 1, 2, 3, 4, and 5 illustrate the changes in flow properties when a commercial calcium soap grease was diluted with 0, 10, 35, 50, and 70% of oil. The effect is substantially a change in yield value only with each addition of oil.

The results at elevated temperatures appear to vary only in degree from those obtained at room temperature. Measurements taken without water in the vicinity of 100° C., where the soap is swollen, show an increased viscosity but no yield value. The addition of water to such a system causes a decrease in viscosity and a marked increase in yield value. On cooling, the yield value is still further increased. The decrease in viscosity is probably due to the coagulative effect of the water. With fatty acid, however, the picture is somewhat different. Initial additions bring about an increased swelling of the soap particles and cause the system to form a more homogeneous mass. With further additions of fatty acid the viscosity reaches a maximum and then decreases as the soap goes into true solution. The yield value in all cases is very small.

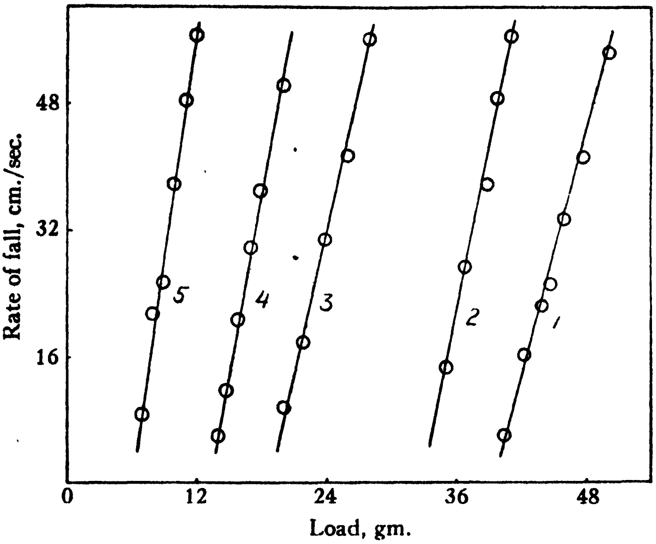

FIG. 5. *Flow–pressure curves for calcium-soap–oil suspensions: 1, 2, 3, 4, and 5, curves for commercial lubricating grease after the addition of 0, 10, 35, 50, and 70% of oil.*

Table I summarizes the effect of the addition of water and fatty acid to dispersions of calcium stearate in oils with viscosities of 300 S.U.S. at 100° F. and viscosity indices varying from 25 to 95. Changes in viscosity of the oil change the slope of the flow–pressure curve but do not influence the yield value. The effect of addition agents is somewhat reduced as the viscosity of the oil is increased, however. The results shown in the table were obtained at room temperature.

Some general observations may be made from these results. The true viscosities of the soap–oil suspensions decrease slightly with increase in the viscosity index of the oil. The addition of water or fatty acid has little effect on this property. The initial yield value is slightly greater if the oil has a viscosity index above 70, and this difference is greatly accentuated by the addition of water. Changes in the yield value due to the addition of fatty acid increase somewhat with increasing viscosity index of the oil. The flow properties of dispersions of calcium stearate in mineral oils with viscosity indices of 70 and 95 are virtually identical provided the viscosities are the same.

TABLE I

THE EFFECT OF ADDITION AGENTS ON THE FLOW PROPERTIES OF CALCIUM STEARATE DISPERSIONS

V.I. of oil	Slope of curve				
	Initial slope	After addition of water	After addition of fatty acid	Change due to water	Change due to fatty acid
25	1.51	1.73	1.86	0.22	0.35
40	1.80	1.97	2.03	0.17	0.23
70	2.33	2.41	1.95	0.08	−0.38
95	2.31	2.41	2.18	0.10	−0.13
V.I. of oil	Yield value				
	Initial yield value	After addition of water	After addition of fatty acid	Change due to water	Change due to fatty acid
25	8.7	8.8	11.5	0.1	2.8
40	8.7	10.5	15.0	1.8	4.5
70	11.3	25.2	15.0	13.9	3.7
95	11.7	25.8	17.7	14.1	6.0

The most outstanding result in these data is the increase in yield value with decreasing polarity of the suspending medium (increase in V.I.) and the accentuation of this property by the addition of water. Since it has been shown previously (4) that small amounts of water have a marked influence on the surface properties and equilibrium sedimentation volume of calcium stearate in oil, this is not unexpected. Highest yield values usually occur where the degree of flocculation of the solid material is greatest, and this condition, as shown by sedimentation experiments, is found with polar solids, where the polarity of the medium is least. The work of von Buzagh (1), who noted quantitatively that the force of adhesion between solid particles suspended in liquid media varied in the same order as the sedimentation volume of the solid, is in agreement with this.

Calcium Oleate Dispersions in Mineral Oils

Since preliminary experiments with a commercial calcium oleate showed it to be unsuitable, the soap used for this work was prepared by neutralizing U.S.P. grade oleic acid with potassium hydroxide in alcoholic solution and reacting the product with an aqueous solution of calcium acetate. After washing, the product was dried at 105° C. and ground to about 200 mesh.

A 40% suspension of this material in a mineral oil with a viscosity of 300 S.U.S. at 100° F. and a viscosity index of 70 gave a flow–pressure curve showing no yield value. With the addition of 1.25% of water based on the soap an immediate yield value of 44 gm. was obtained, and, on standing overnight, the reading rose to about 600 gm. This value was much greater than any obtained with the stearate, and for subsequent experiments it was necessary to cut down the soap concentration to 15%.

Further experiments showed that the use of an oil of lower viscosity index or a small amount of oleic acid with oils of higher viscosity index produced swelling in the soap. The swollen material behaved as a very viscous liquid and no yield value could be found. The addition of water to this viscous mass reduced the viscosity greatly and produced a high yield value. In some instances on the addition of an excess of water the soap became, with agitation, sufficiently lyophobic to give a yield value and viscosity very close to that of the original suspension prior to swelling. In these cases the attraction of the soap particles for one another was largely lost. The reason for this phenomenon is not at all clear, although it appears to be connected with the unsaturation of the acid radical, since it did not occur with the stearate.

Discussion

Microscopic examination of the dispersions of both calcium stearate and oleate after the addition of small quantities of water showed that considerable agglomeration had taken place. This is in agreement with results obtained in the measurement of sedimentation volumes of a number of substances in organic media, after the addition of small quantities of water (3, 4). The effect of other polar non-solvent addition agents, such as glycerol and fatty acid, is similar. It seems probable that after the adsorption of these substances on the polar groups of the calcium soaps, the surface properties are so altered that the attraction between particles of soap is now greater than the attraction between oil and soap, and flocculation takes place. There is thus set up in the system a structure that offers a finite resistance to distortion and gives rise to a yield value. Once this resistance has been overcome, however, the flow–pressure relation is linear. This increase in yield value would scarcely be expected if the increased sedimentation volume were due to the formation of lyospheres, as suggested by Ostwald and Haller (5). Similar results have been obtained with pigments in organic media (2). Since the viscosity of the oil is responsible for the slope of the flow–pressure curve, addition agents will have little effect on it unless they promote swelling.

Systems of this type, although prepared at room temperature with a rather poor dispersion of the soap, probably give a fairly accurate picture of certain steps in the process of grease manufacture. The finished product resembles a commercial grease in texture and appearance, although the consistency is much lower for a given soap content. Flow–pressure curves obtained with diluted commercial greases corroborate this conclusion.

Acknowledgment

This work was carried out under an arrangement between the Imperial Oil Limited and the National Research Council of Canada.

The authors wish to express their thanks to Imperial Oil Limited for permission to publish this paper.

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AN AUTOMATIC BURETTE FOR THE DELIVERY OF GAS AT CONSTANT PRESSURE[1]

BY J. W. HODGINS[2] AND R. B. HARVEY[2]

Abstract

An apparatus has been built to control automatically the addition of gas, from a gas burette, to a system maintained at constant pressure. A phototube-relay, actuated by the mercury level of a manometer connected to the system, acts as the control mechanism for the gas input.

An apparatus has been built whereby known volumes of gas may be added to a system maintained at constant pressure. Taylor and Strother (3) have built a device to maintain a constant pressure in a system. A manometer operates a make and break contact that sets in action a gas electrolysis cell. In this case a fall in pressure causes electrolysis to proceed and restores the gas pressure in the system. Another type of pressure operated relay device has been described by Hoffmann (1) but his apparatus does not allow measurement of the volume of gas being added to the system. Recently Oliver and Bickford (2) published an article on a "Device for Electronic Control of Reduced Pressures" but this apparatus again uses a make and break contact system and a rubber valve. It was felt that any mechanical contact in the manometer or the reaction system should be avoided if possible and, for that reason, a photoelectric system with pressure control by means of interruption of a light beam was selected as the primary control. In Fig. 1 is shown a diagrammatic representation of the system in use.

The operation of the device can be followed by reference to Fig. 1. The bulb, *A*, acts as a reservoir between the burette and the reaction system. The manometer registers the pressure in the system and a stopcock is provided to allow re-evacuation of the zero pressure side of the manometer. The burette, *K*, from which gas is delivered to the system, has a three-way stopcock to allow filling of the burette from a source of supply of the gas, or discharge to the system. The mercury reservoir, *G*, has a flexible connection to permit variations in the mercury level in *G* and *K*. *F* is a pinchclamp operated by the solenoid, *E*, and *H* is a bubble trap to catch any entrained gas bubbles in the mercury. The light source and slit, *B*, are so adjusted that the light passes through the glass manometer arm and falls on the photocell, *C*.* The phototube was mounted at the end of a length of shielded cable to allow it to be moved easily in relation to the light source. The screw, *L*, allows small adjustments of the pressure to be made prior to operation. The light beam should be narrow and parallel to the plane of the mercury meniscus so that sensitivity will be maximum.

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[1] *Manuscript received June 19, 1945.*
Contribution from the Chemical Warfare Laboratories, Ottawa, Canada.

[2] *Captain, Canadian Army.*

* *The phototube-relay system was described in an R.C.A. Bulletin entitled "Phototubes" (Fig. 5, page 10). Any of the numerous phototube-relays mentioned in the literature will serve.*

The action of the apparatus is as follows. With *A* isolated from the system by means of the stopcock, the bulb *A*, the manometer, and *K* are filled with gas at the desired pressure. The pressure is adjusted accurately and the light source levelled with *L* until the mercury meniscus just intercepts the beam falling on the photocell. The stopcock between *A* and the reaction system is opened. Passage of gas out of *A* causes the level of the mercury in the closed manometer arm to fall. The mercury no longer intercepts the light beam falling on the phototube, and the relay is actuated. This causes the pinchclamp to be opened by the solenoid and mercury flows from *G* into *K*. Gas is displaced into the system and the pressure is restored.

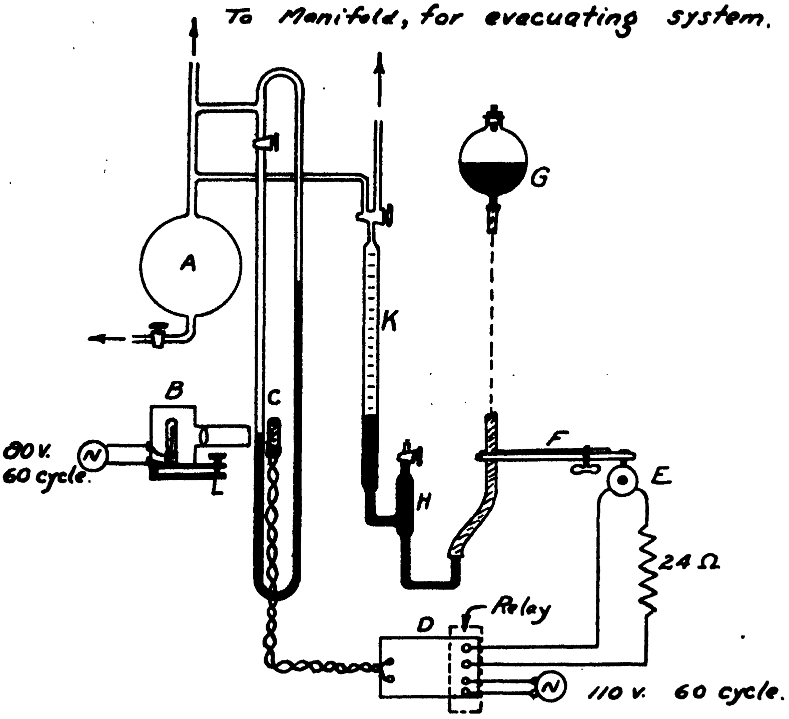

FIG. 1. *Assembly of phototube, manometer, and gas burette.*

Pressure regulation for periods of two hours is good to within ±0.05 mm. For more accurate work it is necessary to insulate the gas-containing apparatus, as room temperature variations may cause the pressure to fluctuate seriously. Reaction pressures are changed simply and rapidly be displacing the light-source–phototube assembly vertically.

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A NOTE ON THE VISCOSITIES OF SOLUTIONS OF NITROCOTTON IN A MIXED NITROGLYCERINE-NITROGLYCOL SOLVENT[1]

By David Fensom[2]

Abstract

Viscosities of solutions of a number of types of nitrocotton in a mixed solvent consisting of 80% glyceryl trinitrate and 20% ethylene glycol dinitrate by weight have been measured in a modified Stormer viscometer. Complete solution was attained only with difficulty, but such solutions when obtained showed viscosity–concentration relations similar to those obtained with acetone solutions.

There is apparently no published information concerning the viscosity of solutions of the various types of nitrocotton in liquid nitric esters. A number of such measurements have recently been made for industrial purposes, and, although no high degree of accuracy is claimed, it is thought that the results may be of general scientific interest. The measurements cover a variety of grades of nitrocotton, made up into solutions in a low-freezing mixture containing 80% by weight nitroglycerine (glyceryl trinitrate) and 20% nitroglycol (ethylene glycol dinitrate).

Experimental Method

For the purpose of these experiments, a Stormer viscometer was modified by replacing the normal steel cup by one of bakelite. Since this cup was slightly conical, and, because of the unknown end effects, conditions of uniform shear were not exactly attained, and measurements of thixotropy (1) could not be made with accuracy. Such considerations were however found to be important only for solutions of the least degraded nitrocottons. The viscometer was calibrated with castor oil at 20° and 10° C., and water and glycerine–water solutions at 20° C., and it is considered that an accuracy of about 5% was normally attained in viscosity measurements.

The nitrocottons used were samples from normal manufacture, and were not specially purified or fractionated. The 80 : 20 nitroglycerine–nitroglycol mixture was also drawn from normal commercial production, and filtered immediately before use. More than one batch of solvent was used in the course of the work. An addition of 0.5% Ethyl Centralite (symmetrical diethyldiphenylurea) was made to the mixtures so that the latter could safely be heated to bring about complete solution of the nitrocotton.

The ingredients of each solution were weighed into an aluminum dish, stirred together for five minutes, and then heated at 60° C. until solution of the nitrocotton was as complete as possible. This was normally the case after about 18 hours, but it should be pointed out that in solutions of some of

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Contribution from the Research Laboratory, I.C.I. (Explosives) Limited, Stevenston, Ayrshire, Scotland.

[2] *At present, chemist, Canadian Armament Research and Development Establishment, M.P.O. 501, Valcartier, P.Q.*

the highest viscosity nitrocottons, a small proportion of partially undissolved nitrocotton fibres could still be observed microscopically after the most prolonged heat treatment. After cooling, the solutions were brought to 20 ± 0.5° C. in the bakelite cups, and the viscosities measured at three or four rates of shear, beginning with the lowest. The results could be reproduced from different samples with a precision of about 10%, the variation apparently being due mainly to the difficulty of ensuring complete solution.

TABLE I

VISCOSITIES OF SOLUTIONS OF NITROCOTTONS IN 80 : 20 NITROGLYCERINE–NITROGLYCOL MIXTURE

Nitrocotton	Concentration, % wt.*	Time of heat treatment at 60° C., hr.	Applied load, gm.	Viscosity, centipoises†
	—	—	50	23.0
HX 3–5	2.00	20	300	86
	4.00	18	300	370
	6.00	18	300	1520
HX 8–13	1.00	18	150	48
	2.00	20	300	113
	4.00	20	300	950
	6.00	18	300	2000
HX 30–50	1.00	18	150	54
	2.00	18	300	181
	4.00	18	300	1260
HL 30–40	1.00	20	300	138
	2.00	20	300	1110
HL 120–170	0.50	18	300	135
	1.00	18	300	400
	2.00	20	300	2520
HM 15–20	0.50	20	300	94
	1.00	20	300	380
	2.00	20	300	4900
HH 5–15	0.50	18	150	150
			300	105
	1.00	18	150	2500
			300	1700
			600	1200
Blasting soluble	0.50	36	150	3050
			300	1670
			600	740
	1.00	36	300	9200
			600	6700
			900	3550

* *Grams per 100 gm. solution.*

† *Single determinations, recorded to three significant figures.*

Discussion of Results

Experimental results are recorded in Table I, whilst the properties of the nitrocottons used are given in Table II. For the sake of brevity, results at several rates of shears are recorded in Table I only, when the variation is greater than can be accounted for by experimental error; in other cases a single viscosity result is given, corresponding to a load of 300 gm., or the nearest load that was practicable experimentally.

TABLE II

PROPERTIES OF NITROCOTTONS USED IN PRESENT WORK

Nitrocotton	Raw material	N_2, %	Viscosity in 95% acetone*	
			Visc., poises	Solute, %
HX 3–5	Cotton linters	11.84	4	40
HX 8–13	" "	11.89	10	40
HX 30–50	" "	11.90	32	40
HL 30–40	" "	11.94	38	20
HL 120–170	" "	12.07	150	20
HM 15–20	" "	11.90	17	10
HH 5–15	" "	11.81	7	3
Blasting soluble	Cotton cops	12.26	140	4

* *Grams nitrocellulose per 100 ml. solvent, 95% by volume acetone, 5% water.*

TABLE III

EFFECT OF HEAT TREATMENT ON VISCOSITY

Solution: 6% HX 8–13 nitrocotton in nitroglycerine–nitroglycol mixture, with addition of 0.5% Ethyl Centralite

Temperature: 60° C.

Time of treatment, hr.	Viscosity, centipoises
1	1130
3	1370
18	1920
36	2120
72	1960
144	1840

A series of results is given in Table III to illustrate the effect of heat treatment on the viscosity of a 6% solution of HX 8–13 nitrocotton. Even at this high concentration, the sample heated for 18 hr. at 60° C., had reached maximum viscosity, thus justifying the adoption of 18 to 20 hr. as the normal maturing period for solutions.

Except at the highest viscosities, the results were in accordance with the empirical Arrhenius equation (3),

$$\eta/\eta^\circ = e^{kC},$$

where η and η° are the viscosities of the solution and pure solvent respectively in centipoises, C is the concentration of solute, in grams per 100 gm. solution, and k is a constant.

This is clear from Fig. 1, in which the logarithm of the viscosity is plotted over the concentration for several series of nitrocotton solutions. Straight lines were obtained with the nitrocottons of low viscosity, but at the higher concentrations of the less degraded nitrocottons the viscosity increase was less than that predicted by the equation. The experimental accuracy was thought to be insufficient to justify attempts to fit the data to more complicated equations.

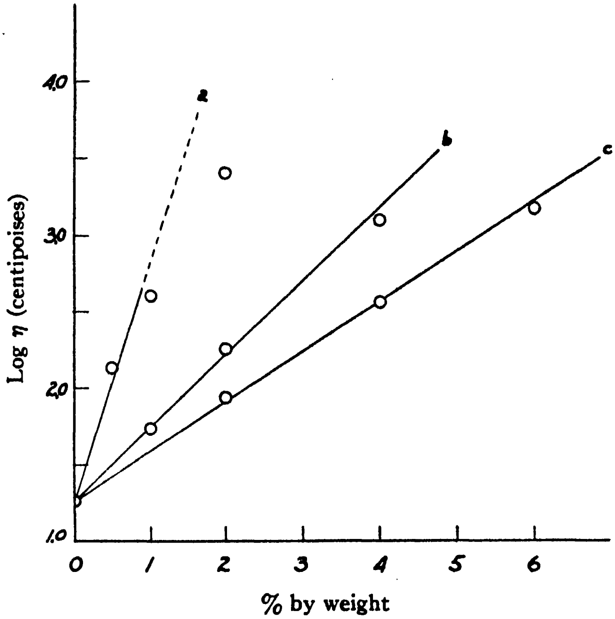

FIG. 1. *Viscosity-concentration curves for nitrocotton solutions. a = HL 120-170. b = HX 30-50. c = HX 3-5.*

Since dilute solutions of nitrocotton in acetone also obey the Arrhenius equation (3), it is of interest to compare the values of the constants k obtained with the same sample of nitrocotton in the two solvents. The graph, Fig. 2, shows the results. Within the experimental error, the values of k obtained with the nitroglycerine–nitroglycol mixture were 1.5 times those obtained with acetone as solvent. The lower values of k obtained in the latter case agree with the relatively higher solvent power of acetone for nitrocotton, the general trend agreeing with that to be expected from the results of work with other solvents (2, 3).

An apparent discrepancy occurs in the case of HH nitrocotton, for which an abnormally low value was obtained with the nitric ester solvent, but the thixotropy shown by solutions of this nitrocotton prevents a true application of the Arrhenius equation. Moreover this nitrocotton was especially difficult to dissolve completely in the nitroglycerine–nitroglycol mixture.

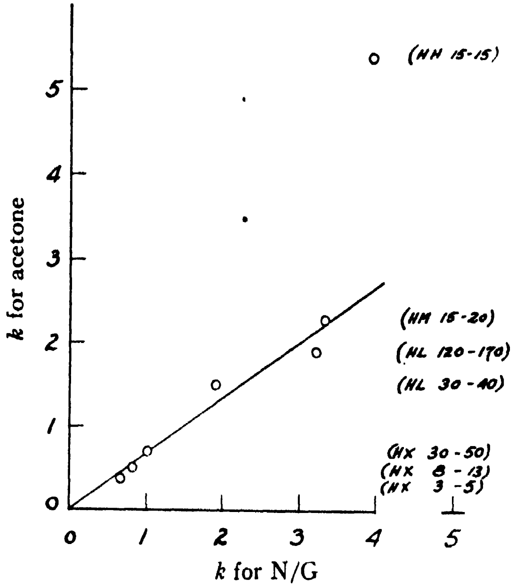

FIG. 2. *Arrhenius constants in acetone and liquid nitric ester.*

From the results obtained, therefore, it may be concluded that although it is difficult to obtain complete solution of nitrocotton in the low-freezing nitroglycerine mixture used in these experiments, yet such solutions when made exhibit viscosity–concentration relations similar to those of solutions of nitrocotton in acetone and other solvents.

Acknowledgment

This work was carried out by the author when a member of the Research Staff of the Research Laboratory of I.C.I. (Explosives) Limited, Stevenston, Scotland, and he is indebted to I.C.I. for permission to publish. He also wishes to acknowledge the assistance of Mr. J. F. Morgan in the preparation of solutions.

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α-CYANO-β-PHENYLGLYCERIC ACID[1]

BY C. Y. HOPKINS[2] AND M. J. CHISHOLM[2]

Abstract

α-Cyano-β-phenylglyceric acid has been prepared by the action of aqueous sodium hypochlorite on α-cyano-β-phenylacrylic acid. It is somewhat unstable and decomposes slowly on standing.

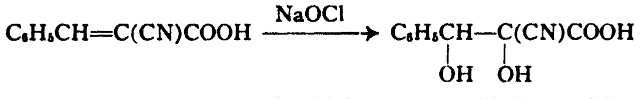
When heated alone, it yields phenylacetic acid. Mild hydrolysis with mineral acid also gives phenylacetic acid. Hydrolysis under special conditions gives phenylpyruvic acid. The mechanism of these changes is discussed.

Theoretical

The reaction of hypochlorous acid or a hypochlorite with substances containing an ethylenic bond usually results in the formation of a chlorohydrin. Unsaturated acids such as acrylic, crotonic, maleic, and cinnamic are readily converted to chlorohydrins.

It was observed by McRae and Hopkins (2) that α-cyano-β-arylacrylic acids did not react with hypochlorite in a normal manner. Alkoxyarylacetic acids were formed when the starting material contained an alkoxyaryl group. α-Cyano-β-phenylacrylic acid itself gave chiefly oils and resinous substances.

It has been found in the present work that α-cyano-β-phenylacrylic acid reacts with sodium hypochlorite solution to give a rather unstable product. By shortening the time of the reaction and avoiding a rise in temperature, it was possible to isolate the substance, α-cyano-β-phenylglyceric acid (I). It has not been described previously.



$$C_6H_5CH{=}C(CN)COOH \xrightarrow{NaOCl} C_6H_5\underset{OH}{\underset{|}{C}}H{-}\underset{OH}{\underset{|}{C}}(CN)COOH \qquad (I)$$

It is apparent that the chlorohydrin, if formed at all, is rapidly converted to the glyceric acid, since no chlorohydrin was isolated in any of our experiments.

α-Cyano-β-phenylglyceric acid exhibits a tendency to decompose on standing and breaks down rapidly when heated in the dry state at 100° C., giving phenylacetic acid. The latter reaction can be shown as resulting from the loss of carbon dioxide and hydrogen cyanide:

$$\underset{\text{(α-Cyano-β-phenyl-glyceric acid)}}{C_{10}H_9O_4N} \longrightarrow \underset{\text{(Phenylacetic acid)}}{C_8H_8O_2} + CO_2 + HCN$$

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[1] *Manuscript received December 21, 1945.*

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1398.

[2] *Chemist.*

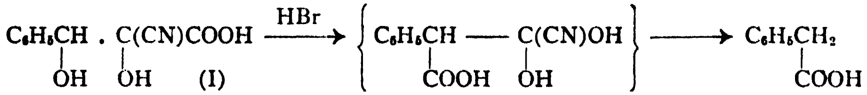
Positive identification of these two gases was made. Water is also produced, indicating that a different mode of decomposition occurs simultaneously. It is judged from inspection of the formula (I) that loss of water would not be compatible with formation of phenylacetic acid.

A quantitative study of the reaction showed that hydrogen cyanide is produced in about one-third the yield calculated from the equation above. Accordingly, it is concluded that, under the conditions of the experiment, about one-third of the material decomposes in the manner indicated and the remainder breaks down in some other fashion with loss of water.

Hydrolysis

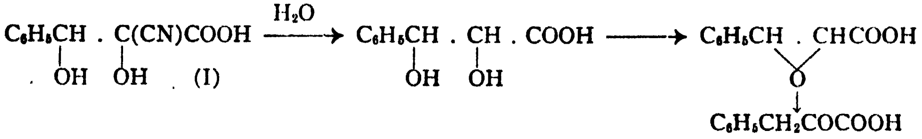
The substance hydrolyses readily under the action of hydrobromic acid. The product is a mixture of phenylacetic and phenylpyruvic acids. By careful regulation of the conditions, the reaction may be controlled to give a good yield of either phenylacetic acid or phenylpyruvic acid as desired.

Using ice-cold 60% hydrobromic acid, the product is mainly phenylacetic acid. The mechanism underlying this change is not immediately apparent. It is possible that the glyceric acid (I) undergoes a pinacolone rearrangement involving migration of the CN, COOH or C_6H_5 group. Migration of the carboxyl group would result as follows:



$$\underset{\displaystyle OH}{C_6H_5CH}\ .\ \underset{\displaystyle OH}{C(CN)COOH}\quad (I)\ \xrightarrow{HBr}\ \left\{\underset{\displaystyle COOH}{C_6H_5CH} — \underset{\displaystyle OH}{C(CN)OH}\right\}\ \longrightarrow\ \underset{\displaystyle COOH}{C_6H_5CH_2}$$

When α-cyano-β-phenylglyceric acid was treated with 52% hydrobromic acid at 25 to 30° C., phenylpyruvic acid was the main product. The yield was good. This procedure constitutes a new method of preparing phenylpyruvic acid. It may be found more convenient than previous methods, which have been described as tedious (1). The reaction is presumably as follows:



$$\underset{\displaystyle OH}{C_6H_5CH}\ .\ \underset{\displaystyle OH}{C(CN)COOH}\quad (I)\ \xrightarrow{H_2O}\ \underset{\displaystyle OH}{C_6H_5CH}\ .\ \underset{\displaystyle OH}{CH}\ .\ COOH\ \longrightarrow\ C_6H_5CH\ .\ CHCOOH\ \ (O)\ \downarrow\ C_6H_5CH_2COCOOH$$

The action of ordinary 48% hydrobromic acid is less satisfactory. The hydrolysis requires several days at room temperature and results in a poor yield of phenylacetic acid.

It was at first thought that phenylpyruvic acid was an intermediate product in the hydrolysis and that phenylacetic acid is the normal end-product. However, upon treating a sample of phenylpyruvic acid with fuming hydrobromic acid, there was no reaction.

It is concluded that acid hydrolysis of α-cyano-β-phenylglyceric acid can occur in two ways. If a pinacolone rearrangement takes place first, the product is phenylacetic acid. If the hydrolysis of the CN group is the initial reaction, the product is phenylpyruvic acid.

Experimental

α-Cyano-β-phenylglyceric acid

α-Cyano-β-phenylacrylic acid (18 gm., 0.1 mole) was dissolved in 450 cc. of water and 75 cc. of 4% sodium hydroxide. The solution was cooled to 20° C. and mixed with 150 cc. of a molar solution of sodium hypochlorite (0.15 mole) also at 20° C.* The mixture was kept at 20° C. for one and one-half hours with occasional stirring, and was finally acidified with dilute hydrochloric acid (1 : 1). The precipitate, which formed gradually, was filtered off after one hour. The yield was 13 gm. When recrystallized from water, it formed glistening flakes, m.p. 88 to 89°†. The substance did not contain chlorine. Found: N, 6.72; equiv. 206. $C_{10}H_9O_4N$ requires: N, 6.76; equiv. 207. These figures taken in conjunction with the products of hydrolysis described below are believed to be sufficient to identify the substance as α-cyano-β-phenylglyceric acid. It is soluble in ethanol and ether, somewhat soluble in chloroform and benzene, and insoluble in hexane.

Upon standing for several weeks in a closed bottle at room temperature, the substance became sticky and finally changed to a thick brown liquid. The liquid had an unpleasant nitrile-like odour.

Hydrolysis to Phenylacetic Acid

A 250 cc. flask containing 10 gm. of α-cyano-β-phenylglyceric acid was surrounded by ice while 95 cc. of ice-cold hydrobromic acid (60% hydrogen bromide) was added slowly. Gas was evolved and a pale yellow precipitate formed. After remaining in the ice-bath for three to four hours, the mixture was diluted and the product was filtered off. It consisted of nearly pure phenylacetic acid (5.0 gm., 75% of theory). After one recrystallization from hexane, it melted at 75 to 76.5° and showed no depression in melting point when mixed with an authentic sample.

Hydrolysis to Phenylpyruvic Acid

Ten grams of α-cyano-β-phenylglyceric acid was mixed with 125 cc. of hydrobromic acid containing 52% of hydrogen bromide. The mixture was maintained at 25 to 30° C. for 24 hr. Phenylpyruvic acid was obtained as a white precipitate (5.0 gm.), m.p. 148 to 153° C. The yield was 60% of theory. After recrystallization from benzene the melting point was 158 to 159° C. The identity of the substance was confirmed by preparation of the acetyl derivative, which had the proper melting point of 172 to 174° C.

Resin was formed when the hydrolysis was carried out at temperatures above 30° C.

Pyrolysis

A weighed sample of α-cyano-β-phenylglyceric acid was placed in a U-tube and heated by a water bath at 90 to 100° C. Nitrogen was passed in and the exit gases were led through a series of absorption tubes. Water was absorbed by calcium sulphate, hydrogen cyanide by $N/2$ silver nitrate, and carbon dioxide by alkali. The hydrogen cyanide was determined by titration. The results are shown in Table I.

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* *A suspension of calcium hypochlorite is equally satisfactory.*

† *Melting points are corrected.*

TABLE I

PYROLYSIS OF α-CYANO-β-PHENYLGLYCERIC ACID

Weight of sample	1.189 gm.	Water	0.076 gm. (74 mole %)
Weight of residue	0.871 gm.	Hydrogen cyanide	0.050 gm. (32 mole %)
		Carbon dioxide	0.166 gm. (65 mole %)
Loss	0.318 gm.		
		Total collected	0.292 gm.

A quantity of the acid was heated *in vacuo* in a short-path distillation apparatus, with the temperature of the heating bath at 90 to 100° C. The condensate amounted to about one-third of the weight of the sample. It was solid and was identified after recrystallization as phenylacetic acid.

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THE EFFECT OF A FOREIGN SUBSTANCE ON THE TRANSITION: NH_4NO_3 IV $\rightleftharpoons$ NH_4NO_3 III[1]

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Abstract

It is shown that the above transition can be repressed (metastably) by using in place of pure ammonium nitrate a solid solution of potassium nitrate in ammonium nitrate. With such a solid solution containing 8 to 10% potassium nitrate, the temperature of the transition III ⟶ IV is depressed to about −20° C. Such solid solutions can be prepared either by fusing the components together or by crystallizing from a mixed aqueous solution.

Introduction

This investigation was undertaken under the auspices of the Associate Committee on Explosives of the National Research Council of Canada. The original problem was to inhibit, over as large a temperature range as possible, the morphotropic change: NH_4NO_3 IV $\longrightarrow$ NH_4NO_3 III. It transpired, however, that this was impossible, but that the converse process of retaining form III in that state far below its normal transition temperature could readily be brought about. We show in this paper that the problem is solved by the use of a solid solution of potassium nitrate in ammonium nitrate. Although this result was obtained by us independently, we subsequently discovered that the same result had been arrived at about the same time by Prof. A. J. Allmand, working in England. Further questions arising out of the work were:— Is it possible to prepare solid solutions of potassium nitrate in ammonium nitrate by crystallizing from aqueous solution, instead of by fusing the components together, and, what is the lower limit of temperature to which the metastability of NH_4NO_3 III can be carried by the addition of potassium nitrate? Finally, is the metastability complete or does form III eventually revert to the stable form IV, in the presence of moisture?

From the point of view of the student of allotropy, ammonium nitrate is one of the most interesting substances. Under ordinary pressure it occurs in no fewer than five polymorphic modifications and, what is still more remarkable, all are stable in their appropriate ranges of temperature, in other words, the phenomena are all those of enantiotropy. Perhaps the best way to designate the forms is by the Roman numerals I to V. According to this classification, the form stable at room temperature is IV, the numbering decreasing towards higher temperature and increasing towards lower. The following table gives the crystallographic description and region of stability of each modification.

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[1] *Manuscript received January 21, 1946.*
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TABLE I

THE MODIFICATIONS OF AMMONIUM NITRATE

Modification	I	II	III	IV	V
Crystal system	Regular	Tetragonal	Rhombic	Rhombic tripyramidal	Tetragonal
Region of stability, °C.	169.6–125	125–83 (84)	83(84)–32	32–(−16) or −18	Below −16 or 18

THE LITERATURE

A very good summary is given in Gmelin's "Handbuch der anorganischen Chemie" (7). In addition to this, the following original papers, which constitute the most up-to-date work on the subject, were consulted. Cohen and van Lieshout (6) find the transition temperature III ⇄ IV as 32.3° C. and this seems to be the best value. Cohen and Heldermann (4) deal with the preparation of the (physically) pure forms of III and IV. Cohen and Kooy (5) had previously found for the densities of the modifications:

$$\text{IV} \quad d^{32.3^\circ}_{4^\circ} = 1.716$$

$$\text{III} \quad d^{32.3^\circ}_{4^\circ} = 1.654.$$

The heats of solution of the two forms, and, hence the heat of transition, are also obtained. Müller (9) shows that potassium nitrate forms solid solutions with ammonium nitrate and that the transition temperature is thereby lowered. The solid solutions used, however, were dilute. A maximum of 0.78% potassium nitrate gave a depression of 1.820° C. Jänecke, Eissner, and Brill (8), in their investigation of the system: NH_4NO_3–$(NH_4)_2SO_4$–H_2O, find that (*a*) the only double salt existing is $(NH_4)_2SO_4 \cdot 2NH_4NO_3$, and (*b*) mixed crystals with ammonium nitrate are formed, whereby the transition temperature is depressed. Wallerant (12), from a crystallographic study, deduces equilibrium diagrams for the binary systems comprising ammonium nitrate and one other alkaline nitrate. The diagrams show a certain lack of knowledge of the phase rule, and from the results of this paper it would appear that he was occasionally dealing with metastable states, but the diagrams are of the greatest interest for the subject of this investigation. In particular, the diagram for the system NH_4NO_3–KNO_3 led to some of the work detailed in this report. According to Wallerant's diagram, the temperature of the transition III ⟶ IV is depressed to subzero temperatures by the addition of about 5% potassium nitrate. This is not true of the stable transition, since the process is not reversible, but it is true metastably. Straub and Malotaux (11), in a short paper, supply the key to the solution of this problem. Using a specialized technique, they determined the transition point of ammonium nitrate containing 1% potassium nitrate in the form of solid solution, with rising and with falling temperature. They found the transition temperature to be, with rising temperature 32.1° C., with falling temperature 23.8° C. According to our work, one figure is too high and the other too low, but the results do show the important fact that form III remains metastable down to a temperature much below its true transition temperature. Sieverts (10) finds that the velocity of transition is somewhat reduced in "ammonpulver", i.e., ammonium nitrate containing carbon.

We attacked the problem along two lines. First, by removing all nuclei of form III, we attempted to preserve form IV metastably above the normal transition temperature. This was found to be practically impossible. Second, we attempted, by forming solid solutions of ammonium nitrate with other substances, such as ammonium sulphate and potassium nitrate, to depress the transition point IV ⇄ III, either stably or metastably, to such an extent that form III became effectively stable at room temperature, and in this latter attempt we succeeded.

Experimental Work

EXPERIMENTS ON PURE AMMONIUM NITRATE

For the determination of transition points it was decided to employ two techniques, viz., the polarizing microscope and the dilatometer. Accordingly, a heated stage was constructed for a polarizing microscope but the instrument was hardly ever used. Unless the crystals are deposited from dilute solution on the microscope slide, they are not usually sufficiently transparent. On the other hand, the dilatometric method showed itself to be sensitive and easy to operate and this technique was therefore exclusively used. The dilatometers, of appropriate size, were constructed by ourselves of Pyrex glass. As inert liquid, toluene, distilled over phosphorus pentoxide, was used.

The experiments with pure ammonium nitrate were based on the well known work of Cohen (4), according to which every normally occurring crystalline form contains nuclei of the other forms which the substance may assume. It was thought that if it were possible to remove from form IV (stable at ordinary room temperature) all nuclei of III, it might be possible to retain IV metastably above its transition point (32.3° C.). It was recognized at the outset, however, that the long and complicated process whereby Cohen (4) obtains the (physically) pure forms was totally inapplicable to industrial work. Another possibility was that commercial ammonium nitrate, as used in explosives, might contain traces of impurity which catalyzed the change. The most obvious of such impurities was water, a well known catalyst for polymorphic changes, and ammonium nitrate is notoriously hygroscopic. However, anything of the nature of intensive drying was likewise out of the question from a commercial point of view.

Chemically pure ammonium nitrate (British Drug Houses, "certified chemical") was used in the earlier experiments. Later on, an 80-pound sack of ammonium nitrate was presented to us by the Consolidated Mining and Smelting Company of Canada, Trail, B.C., and this was used in the later work. The analysis accompanying the sack showed the material to be very pure.

As a first attempt, it was thought that if ammonium nitrate were prepared by crystallization at room temperature, instead of by boiling down, as in commercial practice, such a preparation might consist entirely of form IV, the form stable at room temperature. Accordingly a solution of ammonium nitrate saturated at 20° C. was made up. This was then warmed to 25° C. and filtered six times. It was then placed in a closed container and dried, and filtered air sucked through it. It was found, however, that the vapour pressure of a saturated solution of ammonium nitrate at 20° C. is so low that evaporation by the above process is inappreciable, even after several days. Accordingly, the above preparation was cooled in ice overnight and the resulting crop of crystals filtered in the morning. This crop of crystals was kept at room temperature, first over water, then over sulphuric acid. Two dilatometers were now prepared, one containing 45 gm. of pure, but untreated ammonium nitrate, the other 45 gm. of the above-mentioned ammonium nitrate, which had been left over water for 24 hr., and dried over sulphuric acid for 11 days. Both dilatometers were now placed in a thermostat at 32.0° C. overnight. In the morning, the toluene levels were read on a cathetometer. The temperature was then raised 0.1° C. and kept at that for a further 24 hr. The operations were then repeated. Unfortunately, we were not at this time supplied with completely satisfactory apparatus, and during the fourth night of the experiment the temperature of the thermostat rose to 35.8° C. On checking back to 32.3° C., it was found that the untreated ammonium nitrate had completely transformed, but the treated material only partially so. A repeat of this experiment underwent the same fate, i.e., the temperature of the thermostat rose during the night to 39.5° C., as a result of which the treated specimen had completely transformed. The untreated specimen transformed at 33.0° C. In a third experiment a specimen of ammonium nitrate treated as described above but deliberately moistened with a few drops of water, transformed at 33.6° C.

A sample of ammonium nitrate, recrystallized as described above, was left over water for five days (as recommended by Cohen), then dried over sulphuric acid for 14 days. Two specimens of this lot transformed at 34.0° and 33.0° C., respectively.

It will be seen from the above that our attempted purifications had not resulted in raising the transition temperature more than one or two degrees. In order to determine whether we were really dealing with the (physically) pure form IV, determinations of density were carried out. The material used was recrystallized from water at 0° C., left over water for 24 hr., and dried over sulphuric acid for 11 days. Three determinations of density were made with the following results.

1. $d^{32.2°}_{4°} = 1.7162$
2. $d^{32.3°}_{4°} = 1.7150$
3. $d^{32.0°}_{4°} = 1.7197.$

The untreated ammonium nitrate, dried over sulphuric acid for three days, had a density of $d^{35.8°}_{4°} = 1.6894$.

The above figures are to be compared with Cohen's figure of $d_{4^\circ}^{32.3^\circ} = 1.716$.

A fourth specimen, crystallized as above, and dried over sulphuric acid for 25 days, had a density of $d_{4^\circ}^{32.5^\circ} = 1.7204$. Hence, it appears that our method of preparing form IV is completely successful. Quantitative measurements of the expansion accompanying the transformation also indicated that the preparation was 100% form IV although it may be that, despite the treatment, nuclei of III are still present. Further experiments on pure ammonium nitrate were abandoned, since it appears that even with a form IV that is both chemically and physically pure (and dry), the transition point can be raised (metastably) only one or two degrees. It seems unlikely that the lattice of so soft a substance as ammonium nitrate can permanently resist thermal agitation above its transition point.

EXPERIMENTS WITH AMMONIUM SULPHATE AS ADDITION

These experiments were based on the work of Jänecke, Eissner, and Brill (8), according to which ammonium sulphate forms solid solutions with all forms of ammonium nitrate. Although the stable effect is to lower all transition points, it was thought possible that by rapid chilling, form I, in which the solid solubility is extensive, might be preserved metastably at room temperature. Accordingly, the following procedure was adopted:— A mixture of 3 gm. of ammonium sulphate and 97 gm. of ammonium nitrate was melted carefully with constant stirring; the mixture was completely liquid at 175° C. The molten mixture was then poured into a beaker surrounded by cracked ice, and left until the temperature had fallen below room temperature. This required 30 min. The mass was then ground and dried over sulphuric acid *in vacuo* for 24 hr. A dilatometric experiment was then carried out, the temperature being allowed to rise from room temperature. Transformation took place at 36° to 37° C. Further work with ammonium sulphate was abandoned at this point because of the papers by Wallerant (12) and by Straub and Malotaux (11). According to Wallerant, the temperature of the transition III ⟶ II is raised and that of III ⟶ IV enormously depressed, by the addition of a small quantity of potassium nitrate.

EXPERIMENTS WITH POTASSIUM NITRATE AS ADDITION

If the observations of Wallerant (12) are correct, the effect of the addition of, say, 5% potassium nitrate, is to render form III the only stable form between the ice and boiling points of water; the discontinuous volume change would thus be obviated. According, however, to Straub and Malotaux (11), the stable transition points are not affected to anything like the extent indicated by Wallerant, the observations of Wallerant referring to metastable transitions. It occurred to us, however, that if the metastability were sufficiently obstinate, by adding sufficient potassium nitrate to depress the transition III ⟶ IV (metastably) below room temperature, the reverse transition IV ⟶ III could not, of course, occur, and this we have found to be the case.

Thermal Analyses

The melts of potassium nitrate and ammonium nitrate were first subjected to thermal analysis, employing a sensitive technique, such as is used in metallographic work. The following results were obtained.

Pure ammonium nitrate:

Freezing point = 168.7° C.
Transition I ⟶ II = 125.8° C.
II ⟶ III = Not detectable thermally (some evidence of delayed transition at 64° C.)
III ⟶ IV = 31.2° C.

Pure ammonium nitrate: Substance powdered but not fused, temperature range = 100° to 30° C.

II ⟶ III T = 81.65° C.
III ⟶ IV T = 31.58° C.

1% potassium nitrate: Mixture fused, cooled, powdered, and examined between 100° and 18.5° C.

Possible slow change in the range 90° to 78° C.

III ⟶ IV. Change over range 28.7° to 22.9° C.

Dilatometric Experiments

As the only transitions of importance to this work are III ⟶ II and III ⟶ IV, and these lie within the range of the dilatometer, we returned to this technique. A fused mixture containing 1% potassium nitrate was kept in the ice-chest overnight (maximum temperature = 20° C.). A portion (30 gm.) of this powdered substance was placed in a dilatometer, and the dilatometer filled with dry, ice-cold toluene. The temperature was then allowed to rise from 13.4° C. The transition temperature was found to lie in the range 30.1° to 31.2° C., i.e., a depression of transition temperature of only about 1.7° C. was observed in contradistinction to the very large depression indicated by Wallerant's graph. This, however, is the stable (temperature rising) transition.

It seemed of interest to compare the volume increase accompanying the transformation IV ⟶ III, in the presence of potassium nitrate, with that of pure ammonium nitrate. Accordingly, the total displacement of the toluene column was observed, the radius of cross-section of the capillary measured ($r = 0.04905$ cm.), and the density of the mixture determined. The expansion with pure ammonium nitrate is calculated from Cohen's figures as 3.77%. Our results are:

1% potassium nitrate: Expansion = 2.247%.
2% potassium nitrate: Expansion = 2.574%.

If Cohen's figures are correct, as presumably they are, the volume change is somewhat less, in the presence of potassium nitrate, when the transformation does occur.

The dilatometer experiments were now resumed. With 2% potassium nitrate, the stable (upwards) transition temperature was found to lie at 28.3° C.; the treatment was the same as in the previous case, viz., mixture kept in an ice-chest over night.

4% potassium nitrate: This preparation was treated differently, in that it was never cooled below room temperature (24.5° C.) until the beginning of the dilatometric experiment, when the dilatometer was placed in a bath at 15.9° C. *No transition was observed, up to 88.2° C.* This observation, at first disconcerting to us, receives its explanation from the work of Straub and Malotaux. The sample had never been cooled below the temperature necessary for the (metastable) transition III ⟶ IV. It was, therefore, throughout its history, form III. The temperature of stable transition is extrapolated from the previous results as about 24° C. Another sample of the 4% preparation was kept in a bath at 17° C. for 48 hr. This also showed no transition up to 28.3° C.

The density of the 4% preparation was obtained as

$$d^{32.2°}_{4°} = 1.656.$$

3% potassium nitrate: Kept in bath at 17° C. for 24 hr. Slight indication of transition: $d^{32.3°}_{4°} = 1.6536$.

The preceding experiments having shown that a great difference exists between the transition temperature on heating and that on cooling, a series of dilatometer experiments with falling temperature was now undertaken.

1% potassium nitrate: A new sample was prepared, cooled to room temperature, and ground. A portion (30 gm.) was placed in a dilatometer and the dilatometer kept overnight in a thermostat at 32.3° C. The temperature was then lowered progressively. After the transition with the falling temperature had been observed, the temperature was raised and the reverse transition observed. In solid solution, transition should, of course, take place over a range of temperature, not at a fixed temperature, but under ideal conditions of diffusion, etc., the range should be the same with ascending and descending temperature.

1% potassium nitrate	Temperature falling:	T = 25.3° to 24.9° C.
	Temperature rising:	T = 30.6° C.
2% potassium nitrate	Temperature falling:	T = 20.2° C.
	Temperature rising:	T = 28.3° C.
3% potassium nitrate	Temperature falling:	Transition begins at 18°; becomes rapid around 12° C.
	Temperature rising:	Transition begins at 26°; violent at 27.8° C.
4% potassium nitrate	Temperature falling:	Slight transition at 9.5° C.; increases greatly at 5.6° C.
	Temperature rising:	Transition begins at 23° C.; more marked at 25° C.

5% potassium nitrate Preparation kept overnight at 18° C. Dilatometer heated from 23.45° to 32.2° C.; no transition. Dilatometer then cooled.

Temperature falling: Transition seemed to begin around 1° C. Dilatometer kept in cracked ice overnight.

Temperature rising: Transition at 22° C.

Analysis of Specimens

The mixtures described as 1%, 2%, etc., potassium nitrate were made up synthetically. Owing to volatilization and decomposition of the ammonium nitrate on melting, the compositions were not precisely those of the original weights. The mixtures were therefore analysed by converting the potassium nitrate to potassium sulphate. The method is not very sensitive and the error large, but the results are probably good enough for the work in hand. The results are:—

Nominal KNO_3 content, %	True KNO_3 content, %
1	0.986 ± 0.073
2	1.965 ± 0.084
3	3.163 ± 0.075
4	4.405 ± 0.115
5	5.126 ± 0.171

Densities of the Potassium Nitrate Solid Solutions

As the densities given above were determined without reference to the previous thermal history of the sample, they must be considered as more or less meaningless in the light of what has been said about the metastability of the transformation. The present work was designed to take into account the previous thermal history, and to act as a check on the dilatometer results.

Two hundred grams of each of the mixtures was prepared by fusion and subsequent slow cooling. This was ground, dried over sulphuric acid for 24 hr., sealed off in glass flasks, and kept in a thermostat at 32.3° C. for five days. Each mixture should then have been in the stable III condition. The density of each sample was then determined as follows:

KNO_3 content, %	$d^{32.3°}_{4°}$
0.989	1.620 : 1.616
1.965	1.647
3.163	1.651
4.405	1.664
5.126	1.671

If these figures are graphed, the density of 2% potassium nitrate is seen to be distinctly too high for a straight line relation. Since all the preparations are in the condition of form III and potassium nitrate is somewhat denser than ammonium nitrate, it is apparent that the formation of solid solutions in form III is attended by considerable expansion.

The temperature of the thermostat was then lowered to 22.55° C., at which temperature 1% potassium nitrate should have transformed to form IV but the others not.

The following figures were obtained:

KNO_3 content, %	$d^{22.55°}_{4°}$
0.980	1.6602
1.965	1.6313
3.163	1.6494
4.405	1.6611
5.126	1.6667

Somewhat surprisingly, the figures at the lower temperature are, with the exception of those for 1% potassium nitrate, slightly lower than those at 32.3° C. This may be error or it may be real, indicating some slow progressive change in the solid solution. The important thing, however, is the marked increase in density of the 1% potassium nitrate, indicating that this solid solution alone has passed the transition III $\longrightarrow$ IV. The increase in density, about 4 units in the second decimal place, is too large to be experimental error, but is still somewhat less than the change of density of pure ammonium nitrate (about 6 units in the second decimal place). This is in agreement with our direct observation of the volume change accompanying the transition, which we found to be distinctly less than with pure ammonium nitrate. Again, it is to be observed that the density of the transformed 1% potassium nitrate is also much less than that of pure ammonium nitrate in the same condition, indicating that potassium nitrate also forms solid solutions with form IV, and that these solid solutions are also formed with expansion.

As a check on the rapid work of the dilatometer, various solid solutions were kept in the thermostat at different temperatures for long periods, and the density determined. The transition would thus manifest itself as an abrupt change in density; at this time we still feared that the metastability might only be a question of time. The solid solutions were kept over concentrated sulphuric acid for 24 hr., then sealed off in glass flasks, and kept in the thermostat at 32.3° C. for five days. Samples were then removed for density determination and the flasks resealed. The temperature was then lowered to 22.55° C. (i.e., a temperature below the transition point of 1% potassium nitrate as determined by cooling in the dilatometer), kept at that for 24 hr., and the densities then determined. This procedure was then first repeated at 18.1° C. for 48 hr., and then finally in cracked ice overnight. The results are contained in Table II.

TABLE II

DENSITIES OF AMMONIUM NITRATE AT DIFFERENT TEMPERATURES

Temp., °C.	Potassium nitrate, %				
	1	2	3	4	5
	Density, d_4^t				
32.3	1.620 1.616	1.647	1.651	1.664	1.671
22.44	1.660	1.631	1.649	1.661	1.667
18.1	1.655	1.676 1.678	1.659	1.661	1.668
0.7		1.679	1.697	1.686	1.719

There are some discrepancies in the above figures, either due to experimental error (included air?) or to some slow secular change in the solid solution, but the qualitative result is the same as with the dilatometer, viz., the 1% potassium nitrate has undergone transformation at 22.5°, the 2% at 18.1°, the 3% partially at 18.1°, but completely at 0°, while the 4 and 5% had also changed completely at 0° C.

Analysis of Solid Solutions Prepared by Fusion

Six new preparations were made (1, 2, 3, 4, 5, and 6% potassium nitrate), ground, preserved over concentrated sulphuric acid, and analysed for potassium nitrate by conversion to potassium sulphate. The results were:

Nominal KNO_3 content, %	True KNO_3 content, %
1	0.9517 ± 0.0162
2	1.737 ± 0.008
3	2.780 ± 0.084
4	3.931 ± 0.06
5	4.741 ± 0.01
6	5.839 ± 0.014

Protracted Dilatometric Experiment

With the idea that the metastability might not really be permanent, we started the following experiment. New samples were prepared of 1 to 6% potassium nitrate and 10% potassium nitrate. These were dried over sulphuric acid for several days. Samples (30 gm.) of each were then placed in separate dilatometers, which were filled up with toluene that had been dried over phosphorus pentoxide. These dilatometers were then left in a thermostat at 32.3° C. overnight. They were thus all in the III condition at the start of the experiment. This experiment was begun September 26, 1941. After reading the toluene levels at 32.3° C. the thermostat temperature was lowered 1° to 31.3° C. and maintained at that value for 24 hr. On the following morning the toluene levels were again read, the temperature then lowered 1°, and so on.

On October 10, the 1% potassium nitrate transformed at 26.2° C. On October 21, the 2% potassium nitrate transformed at 21.3° C. By October 30 the temperature had been dropped to 16.3° C. and the temperature was kept at that value until January 9, because we had no means of obtaining a controlled temperature below 16.3° C. During this period, the 3% potassium nitrate underwent slow transformation. A cooling unit with thermostatic control was put into operation on January 9, and the temperature dropped 1° C. per day, as before. On February 10, the 4% potassium nitrate transformed together at 2.0° C. By February 28 the temperature had been lowered to −0.6° C., the 10% potassium nitrate (dry) and the 10% potassium nitrate (moist) remaining untransformed. On March 2, the "10% potassium nitrate moist" (1.7% H_2O) transformed at −0.1° C. after a week at this temperature. The "10% potassium nitrate dry" remained untransformed at −10.0° C. This confirms Allmand's statement that the stability is considerably reduced by the presence of moisture (*vide infra*).

Dilatometric Experiment with 10% Potassium Nitrate

In order to avoid the necessity of adding or abstracting toluene from a dilatometer with capillary bore, a dilatometer with relatively wide bore (about 2 mm.) was constructed and charged with 30 gm. of 10% potassium nitrate in solid solution. The sensitivity was much reduced by this procedure but it was calculated that total transformation (corresponding to a volume change of about 3%) would produce a displacement of several centimetres. With this apparatus it was possible to investigate between 95° and 0° C., without removal or addition of toluene. Starting from 20° C., the temperature was raised to 95° C., then lowered to 0° C., the whole operation occupying about three hours. No transition was observed.

EFFECT OF MOISTURE

According to Allmand (confidential report) if the moist sample is submitted to a cyclic treatment, that is, alternately heated to 55° C. and cooled to −20° C., an expansion (presumably representing partial transformation) occurs; the expansion is much less than corresponds to complete transformation. Our experiments had been carried out with well dried specimens, and even the toluene used was distilled from phosphorus pentoxide. Accordingly, two dilatometers were prepared, one filled with a sample of commercial ammonium nitrate which had been dried for six months over concentrated sulphuric acid, and which therefore approached to an intensively dried specimen, and the other with a sample of the same material to which 1 cc. of water had been added (charge, 30 gm.). The following were the results:—

Sample	Transition temperatures, °C.	
	Temp. rising	Temp. falling
Moist	34.9	28.9 : 30.2
Dry	34.9	29.2 : 30.4

It appears that in the case of pure ammonium nitrate, presence or absence of moisture has little effect, and this confirms our previous results.

It appears that Allmand's observations were carried out on compressed blocks and it is possible that the observed expansion is to be attributed to the interstices of the material. This effect would not be observed in the NH_4NO_3–KNO_3 mixed crystals in powdered form. Accordingly a 10% potassium nitrate (prepared by fusion) was introduced into a dilatometer having a wide bore and furnished with a reservoir at the top; the instrument was then sealed off at the top. Dilatometric readings were taken up to 95.0° C. and down to 0.1° C.; there was no evidence of a transition. Apparently the transition III ⟶ II is raised above 84° C., which is the value for pure ammonium nitrate.

To investigate the effect of moisture two dilatometers were filled, one with commercial ammonium nitrate which had been dried out for six months over concentrated sulphuric acid, the other with the same material which had been moistened. The following are the results:

——	Transition begins	Trans. max. velocity
	Temperature falling	
Dry NH_4NO_3	29.7° C.	29.2° C.
Moist NH_4NO_3	29.4°	28.9°
	Temperature rising	
Dry NH_4NO_3	34.9°	34.9°
Moist NH_4NO_3	34.35°	34.9°
	Temperature falling	
Dry NH_4NO_3	30.85°	30.4°
Moist NH_4NO_3	30.85°	30.2°

The presence of moisture seems to have little effect on the hysteresis, although, of course, it is quite possible that the so-called "dry" sample still contained a trace of moisture.

Two dilatometers were now prepared with reservoirs at the top. These were charged with 10% potassium nitrate (prepared by fusion), one sample being "dry" the other being "moist". After addition of the indicator fluid (xylene) the dilatometers were sealed off. These were stabilized in a thermostat at 16° C. overnight. They were then heated to 50° C. and cooled to −20° C. (ice and salt) on alternate days; they were brought back to 25° C. each night, kept in the thermostat overnight, and the levels read the following morning. Three such complete cycles were carried out. The results were surprising. A *contraction* was observed, amounting to 0.38% for the dry specimen, and to 0.17% for the moist. Most of the contraction was observed in the first cycle. This was, however, probably a malobservation, for xylene was observed to have condensed in droplets in the reservoirs. In the calculation of the above contractions, the density of 10% potassium nitrate was determined as $d_{4°}^{25°} = 1.682$.

The preceding experiment was therefore repeated using sealed dilatometers without reservoirs, it having been found that the diameter of the dilatometer (about 1 mm.) was sufficient to take up the expansion. Care was taken to remove all trace of included air. Four complete cycles were carried out. The moist sample, in this case, showed a contraction of 0.4%, the dry sample no contraction at all. In view of the irregular nature and small amount of the effect we are inclined to attribute it to secondary causes, probably dissolved air. The probability is that 10% potassium nitrate *per se* shows no permanent volume change. Nevertheless, as shown above, a solid solution containing as much as 10% potassium nitrate will eventually transform below 0° C., if it is moist and if it is kept sufficiently long at that temperature (say −10° C.).

EFFECT OF SODIUM NITRATE IN THE PRESENCE OF POTASSIUM NITRATE

A ternary mixture of composition 72% ammonium nitrate, 20% sodium nitrate, and 8% potassium nitrate froze at the eutectic temperature of 117.5°C. We thought this might represent a convenient method of preparing the NH_4NO_3–KNO_3 solid solutions. A dilatometer was charged with this eutectic mixture and an experiment carried out. The dilatometer was allowed to cool from 130° C. Allotropic transformation, no doubt III ⟶ IV, took place at 12° C. Apparently the presence of the sodium nitrate prevents the potassium nitrate from exerting its effect. The explanation is no doubt as follows. It is known that sodium nitrate and potassium nitrate form a continuous series of solid solutions above 130° C. (2). Below this temperature the solid solution breaks up into a conglomerate but the liberated potassium nitrate will not be entirely taken up by the ammonium nitrate, since the system is now largely solid. In other words, the content of potassium nitrate in the NH_4NO_3–KNO_3 solid solution is less than appears from the total potassium nitrate content, and hence the depressing effect on the transition temperature is not so great. The desired effect could no doubt be obtained by using a higher proportion of potassium nitrate.

Preparation of NH_4NO_3–KNO_3 Solid Solutions from Aqueous Solutions

The question as to the possibility of preparing solid solutions of potassium nitrate in ammonium nitrate, from the corresponding aqueous solutions, has already been answered in the affirmative, more or less, by the work of Caillart (3) and of Ando (1), who studied the system KNO_3–NH_4NO_3–H_2O at temperatures of 17° and 25° C. From the results of both it appears that mixed crystals of the ammonium nitrate type, containing up to about 30% potassium nitrate, can be obtained by crystallization from mixed solutions, and that the solid solution obtained is not greatly different in composition from the equilibrium aqueous solution. These results for room temperature do not necessarily apply to the temperatures of industrial crystallization, so the following experiments were carried out. A mixture of the following composition:— 2720 gm. ammonium nitrate, 272 gm. potassium nitrate, and 1380 cc. water (total volume = four litres), was made up to a clear solution, and boiled down to about two-thirds bulk. The initial boiling point was 129° C., rising finally to 141° C. The solution was allowed to cool overnight, filtered by suction, and the crystals pressed and weighed, as was also the residual mother liquor.

Weight moist crystals = 2792 gm.
Weight mother liquor = 386 gm.
Therefore, wt. water evaporated = 1194 gm.
Ratio of $NH_4NO_3 : KNO_3$ = 7.25 : 1.

The mass of crystal was ground and mixed, and a sample analysed for potassium nitrate, ammonium nitrate, and moisture.

First experiment

Analysis of crystals

H_2O = 4.27%
KNO_3 = 7.85%
NH_4NO_3 (Kjeldahl) = 88.08%
Ratio $NH_4NO_3 : KNO_3$ = 11.2 : 1 by weight

Analysis of mother liquor

KNO_3 = 4.52%
NH_4NO_3 = 62.2%
Ratio $NH_4NO_3 : KNO_3$ = 13.8 : 1

Second experiment

Original solution NH_4NO_3 = 2961 gm.
KNO_3 = 592 gm.
Volume = 4 litres

This solution began to boil at 110° C. and was evaporated until the boiling point rose to 120° C.

Wt. moist solid phase = 1679 gm.
Wt. mother liquor = 1898 gm.

Analysis of crystals

H_2O = 3.60%
KNO_3 = 19.00%
NH_4NO_3 = 78.1%
100.7%
Ratio $NH_4NO_3 : KNO_3$ = 4.1 : 1.

Analysis of mother liquor

NH_4NO_3 = 56.58%
KNO_3 = 10.31%
Ratio $NH_4NO_3 : KNO_3$ = 5.5 : 1

The above agrees with the results of Caillart, and of Ando, and also of Allmand.

HOMOGENEITY OF SOLID SOLUTIONS PREPARED IN THE WET WAY (BY CRYSTALLIZATION FROM AQUEOUS SOLUTION)

The solid solution containing 7.8% potassium nitrate was submitted to dilatometric investigation. It was found to transform, on cooling, at 21.6° C. Had such a preparation been homogeneous, it would not have transformed above 0° C. On repeating the experiment, transformation occurred at 12.6° C. It is noteworthy that this sample was prepared by boiling down a solution almost to dryness, i.e., the total mass of mixed crystals was much greater than the residual mother liquor. Under these circumstances it is perhaps not surprising that the product was not homogeneous. Accordingly a third preparation was made in the following manner:— A solution of original composition 48.8% ammonium nitrate and 11.48% potassium nitrate began to boil at 110° C., and was evaporated till the boiling point rose to 115° C. A crop of 303 gm. of crystals was obtained, and a mother liquor of 3550 gm. Analysis of these gave the following values:

Constituent	Crystals	Mother liquor
NH_4NO_3, %	70.5	52.95
KNO_3, %	27.2	11.34

This preparation showed no transformation between 40.6° and 0.8° C. Such a solid solution is, however, unnecessarily high in potassium nitrate. Accordingly, a fourth preparation was made by boiling down an original solution containing 43.95% ammonium nitrate and 5.115% potassium nitrate. Boiling began at 109° C. but no crystals were obtained up to 117° C. Further evaporation was continued to 119° C. Yields of 378 gm. of crystals and 1570 gm. of the mother liquor were obtained. The analyses were:—

Constituent	Mother liquor	Mixed crystals
NH_4NO_3, %	57.92	87.2
KNO_3, %	6.42	13.19

This preparation showed no transformation between 38.7° and 0.9° C.

Summary of Results

Owing to the nature of this work, which was dictated by practical considerations rather than any prearranged and systematic scheme, much of the discussion is necessarily included with the experimental results, and the reader is referred to that section. The main result of the work is that a solid solution of potassium nitrate in ammonium nitrate, containing, say, 5% potassium nitrate, can be kept indefinitely in form III (instead of the stable form IV) at room temperature. Such a solid solution can be prepared by melting up the weighed components at the lowest possible temperature (about 175° C.), with stirring to ensure homogeneity. This homogeneous liquid is allowed to solidify and to cool to room temperature slowly. The resulting mass will show no discontinuous volume change between 0° and 100° C. It is quite insufficient merely to mix the potassium nitrate with the ammonium nitrate: the mass must be melted up (or crystallized from solution) to produce solid solution.

Solid solutions of potassium nitrate in ammonium nitrate can readily be prepared by crystallization from a mixed aqueous solution.

Below 0° C., the metastability is less pronounced. Even a solid solution containing as much as 10% potassium nitrate will eventually undergo transformation, if it is kept long enough at, say, −10° C., particularly if it is moist. On the other hand, the results of Professor Allmand with compressed blocks, according to which, on "cycling", i.e., alternately raising and lowering the temperature, the blocks undergo a progressive expansion, appear to us to be due to a disruption of the blocks, rather than to morphotropic change. In any case, the change III $\longrightarrow$ IV is accompanied by contraction.

The effect of moisture in catalyzing the change has been demonstrated below 0° C.: above that temperature, it seems to be powerless to destroy the metastability.

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THE PORE STRUCTURE AND ADSORPTIVE PROPERTIES OF SOME ACTIVATED CHARCOALS

I. THE ADSORPTION OF WATER VAPOUR AND ITS DEPENDENCE ON PORE SIZE[1]

By M. N. FINEMAN[2], R. M. GUEST[3], AND R. McINTOSH[4]

Abstract

An examination of the influence of the structure of charcoal adsorbents on the form of the water adsorption isotherm has been attempted by determinations of (1) surface areas of a series of charcoals of varying degrees of activation using nitrogen and butane as adsorbates; (2) total pore volume of each adsorbent sample by density measurements in helium and in mercury; (3) density of adsorbents when immersed in water; (4) adsorption isotherms for water vapour; and (5) surface areas of charcoals partly saturated with water vapour.

The evidence appears to suggest that certain very small and certain very large voids in charcoal are not occupied by water vapour at any value of the relative pressure. The former, 10% by volume, are important in terms of surface area; the latter, 30% by volume, influence pore volume calculations. An explanation of the shape of the water adsorption isotherm is attempted in the light of these facts. Estimates of the submicro, micro, and macro pore sizes show fair agreement when these are based upon either the capillary condensation theory or measurements of the total area and volume of the charcoal pores.

Introduction

When one considers the adsorptive properties of activated charcoal, it is at once apparent that the mechanism by which water vapour is taken up is in some way distinct from that for most other vapours and gases. In nearly every other instance the adsorption isotherm of the gas may be described analytically by an equation of the Langmuir type. In the case of water vapour, however, the form of the curve is that classified by Emmett and his associates as a Type V isotherm (9, pp. 1–36). In contrast with the Langmuir adsorption isotherm, very little adsorption is found at low values of relative pressure, and the greater part of the adsorption occurs over a narrow relative pressure range. Moreover, adsorption is not marked near saturation pressures, and the curve does not approach the weight axis asymptotically near a relative pressure value of 1 (20, pp. 143–154).

From the viewpoint of the Brunauer, Emmett, and Teller theory of multilayer adsorption (6), such a curve is explained on the assumption that $E_1 < E_L$, where E_1 and E_L are the energy of adsorption in the first layer and the energy of liquefaction, respectively. The region near saturation must be explained on the assumption that all the voids have been filled, and that bulk condensation on the surface does not occur. On the other hand, the form of the curve may also be interpreted from the older conception of capillary condensation.

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Here, too, certain regions of the isotherm are not easily reconciled with theory. In the first place, since the structure of the adsorbent may be expected to contain channels of dimensions ranging from those less than molecular dimensions to those of very large diameter, the extremely small amount of adsorption at low relative pressures would not be anticipated, unless the total volume of the small pores is negligible. Near saturation a marked increase in amount adsorbed would be expected for an adsorbate whose wetting angle with the solid is zero.

In favour of the capillary condensation theory is the phenomenon of limited hysteresis. It has been found by many observers that the adsorption–desorption curves for water do not correspond over a wide range of relative pressure. Attempts to explain this phenomenon by the presence of inert permanent gases (20, pp. 143–154), alteration of the wetting angle on desorption (1–4, 12), the form of the internal voids (19, Chap. XX, p. 1661), have frequently been made. One of the most plausible of these has recently been put forward by Cohan (7, 8) on the assumption that condensation occurs along the walls of the interstices in an annular ring, while desorption occurs from a hemispherical meniscus. These considerations alter the form of the equation relating condensation pressure and capillary radius by a factor of 2, which accounts for the hysteresis.

Kelvin equation: $$\ln \frac{P_r}{P_0} = \frac{-2\sigma \bar{v} \cos \theta}{rRT} \tag{17}$$

Cohan equation: $$\ln \frac{P_r}{P_0} = \frac{-\sigma \bar{v} \cos \theta}{rRT} \qquad (7,\ 8)$$

where P_r is vapour pressure over capillaries of radius r,
P_0 is vapour pressure at saturation,
σ is surface tension,
$\bar{v}$ is molal volume,
θ is angle of contact.

Important also is the deduction that no hysteresis will occur in voids whose diameter is less than four molecular diameters, for in this case the two equations will coincide. This prediction has received some measure of confirmation from experiment, since the adsorption–desorption curves frequently coincide at relative pressures less than 0.4 (10).

It should be emphasized that, to our knowledge, no experiment has yet been devised that will serve to distinguish clearly between the various viewpoints. Nor has such an experiment been carried out in this investigation. However, evidence has been accumulated that may be utilized in explaining the anomalies arising from the application of the capillary condensation theory. In the first place, definite evidence is provided that certain of the voids of the adsorbent are not occupied by water at any value of the relative pressure. These voids appear to be of two types: very small in diameter and quite large in diameter. The very small voids contribute little to the total pore volume of the sample, but are of importance in terms of the surface area as measured by adsorption of nitrogen at liquid oxygen or liquid nitrogen temperatures. The large pores are relatively important from the standpoint of pore volume, but unimportant in terms of surface area. Water vapour is apparently adsorbed in voids of intermediate dimensions; this accounts for the narrow range of adsorption in terms of relative pressures. The fact that large pores do not fill up with adsorbate clearly suggests that the wetting angle between solid and adsorbed material is greater than zero. Somewhat similar views have been arrived at independently by Pierce and Juhola and their associates (23).

In this investigation a somewhat more careful examination of the influence of the structure of the adsorbent on the form of the adsorption isotherm has been attempted than in earlier work. The methods used were straightforward. They consisted of (*a*) determination of the total surface area of a series of charcoals of varying degrees of activity, using two adsorbates, nitrogen and butane (the latter was chosen to demonstrate the influence of molecular size); (*b*) determination of the total pore volume of each sample by measurements of the density of the adsorbent in helium and in mercury; (*c*) measurement of the density of the adsorbent when immersed in water; (*d*) determination of the adsorption isotherm for water; and, finally, (*e*) several preliminary determinations of surface area on charcoal samples partly saturated with water vapour.

Since the experimental procedures for most of these measurements are well known, they will not be described in detail. The procedure for determining (*c*) has been described fully in another paper of this series (11).

Experimental

(*A*) *Surface Areas*

The surface areas were measured by the method of Brunauer, Emmett, and Teller (6) in a standard type of adsorption apparatus. Except for Sample *G*, all samples showed monomolecular adsorption according to the criteria of the method. Using nitrogen, some were tested both at liquid oxygen and liquid nitrogen temperatures. The areas measured at the two temperatures agreed within the expected reproducibility of the measurements. The dead space of the adsorption cell was measured with purified helium at the temperature of the adsorption measurement, on the assumption that helium is not adsorbed to an appreciable extent (13, 14, 16). A standard procedure of preparing the charcoal sample was used throughout. It was evacuated at 110° C. until the pressure was between 10^{-4} and 10^{-5} mm. of mercury at that temperature with the pump shut off. No attempt was made to remove inorganic matter. Corrections for deviations from the ideal gas law were applied in all the adsorption experiments.

(*B*) *Determination of the Density in Helium*

The experimental arrangement for determining the density in helium was almost exactly similar to that of Howard and Hulett (15). Evacuation of the samples was carried out as described above, and purified helium was employed. No drift in the density value with time was observed if the purification was properly carried out, a result that does not agree with the observation of Howard and Hulett on the carbons employed by them.

(*C*) *Determination of the Density in Mercury*

The density of the samples in mercury was readily determined by means of a pycnometer arranged so that after evacuation the volume of a known weight of carbon could be read directly on a burette as the difference between the volume of the container when empty and when partially filled by the carbon sample. The final volume reading was made under conditions such that the pressure of mercury on the sample was approximately ½ atm. Since mercury may be forced into the larger voids by pressure, a small error is introduced by this method of measurement. However, similar determinations in a different form of apparatus where the effective pressure of mercury is approximately 1½ atm. (22) shows that this error is less than 3 to 5%.

(*D*) *Determination of the Density in Water*

The density of the samples in water was found in a special form of pycnometer (11). The carbon was thoroughly evacuated before being wetted, and the equilibrium value of the density determined.

(*E*) *Water Adsorption Isotherms*

The water adsorption at 20° C. was determined by the gain in weight of the sample after equilibrium had been established between the sample and a sulphuric-acid–water solution of known density. Evacuation of the sample was carried out as previously described. The sulphuric-acid–water solutions were freed of gases by repeated freezing and evacuation. The density of the solution was determined after equilibrium with the samples had been attained. The adsorption balance was similar to that of McBain and Bakr (21), except that the spiral was made of 32 gauge phosphor-bronze wire. The spirals were about 8 cm. long and 0.4 cm. in diameter, with about 40 turns per cm. The calibration of the spiral was determined after the evacuation at 110° C. to correct for possible deformation when heated under strain. The reproducibility of the measurements was less than would be expected from the sensitivity of the spirals. This may have been due to variations in the thermostat control or to the length changes that would be caused by fluctuations in room temperature, since an appreciable length of the spiral system was above the thermostat liquid level. With measurements reproducible to 0.005 cm. on the cathetometer, these spirals could support about 10 gm. without exceeding their elastic limit. On the average, 1 gm. weight caused an extension of about 2.5 cm. Despite temperature variations, the values indicated are believed sufficiently accurate, so that the comparisons that are made later are substantially correct.

Limited hysteresis of the water isotherms was found with these samples. No thorough examination of the hysteresis loops was attempted, and the data are therefore not included. The existence of hysteresis, as emphasized in the introduction, is most readily explained on the basis of the capillary condensation theory.

(*F*) *Carbon Samples*

The carbon samples *A* to *F*, inclusive, were made by the steam activation of cocoanut shell at the Standard Chemicals Co. Ltd., Montreal. The samples were obtained from a single furnace charge. A grab sample of the charge was taken at intervals of 12 hr. The grab sample was then screened and material of 8 to 14 mesh collected for study. The ash content of these materials is approximately 0.5% (22):

Sample *G* is a zinc chloride activated material obtained from the National Carbon Company. The ash content of this sample is about 2%. If volatilization of zinc chloride occurs during the combustion test, the amount of inorganic material in the untreated sample will be somewhat greater than this figure (22).

Results

Surface Areas

The surface areas of the samples using both butane and nitrogen are given in Tables I and II. The Langmuir form of adsorption isotherm is clearly

TABLE I

AREA AVAILABLE TO NITROGEN AT 90.1° K.

Sample	Time in furnace, hr.	v_m* cc./gm.	Surface area, sq. m./gm.	$(E_1 - E_L)$	E_1
				Kcal. per mole	
A	12	14_0	64_4	0.8_9	2.2_2
B	24	16_3	74_9	0.9_6	2.3_8
C	48	19_5	89_5	0.8_6	2.1_9
D	72	20_1	96_3	0.9_7	2.2_9
E	96	23_8	107_0	0.8_8	2.2_1
F	120	24_7	113_6	0.9_1	2.2_4

*v_m *is the volume of adsorbate that covers the surface with a monolayer.*

TABLE II

AREA AVAILABLE TO BUTANE AT 0° C.

Sample	v_m cc./gm.	Area (*a*)*	Area (*b*)**	$(E_1 - E_L)$	E_1
		Sq. m./gm.		Kcal. per mole	
A	$38._8$	33_3	50_0	2.0_0	7.3_0
B	$48._0$	41_7	62_5	2.0_0	7.3_0
C	$63._6$	55_3	82_9	2.1_0	7.4_0
D	$69._3$	60_2	90_3	2.1_9	7.4_9
E	$80._9$	70_8	105_0	2.1_0	7.4_0
F	$84._9$	73_7	110_0	2.2_6	7.5_6

* *Area (a). Butane molecular area = 32.1 sq. Å.*
** *Area (b). Butane molecular area = 48.0 sq. Å.*

shown by the linearity of the plots in Figs. 1 and 2. An area of 17.0 sq. Å is assumed for nitrogen at 90° K. and 16.2 sq. Å at 77° K. For the butane adsorption at 0° C. two values for the area of the butane molecule have been used, because of the uncertainty concerning its accuracy (10). These values are 32.1 sq. Å and 48.0 sq. Å, respectively.

To show the influence of the size of the adsorbate molecule on the determined area, the ratio of the area values obtained using nitrogen to those

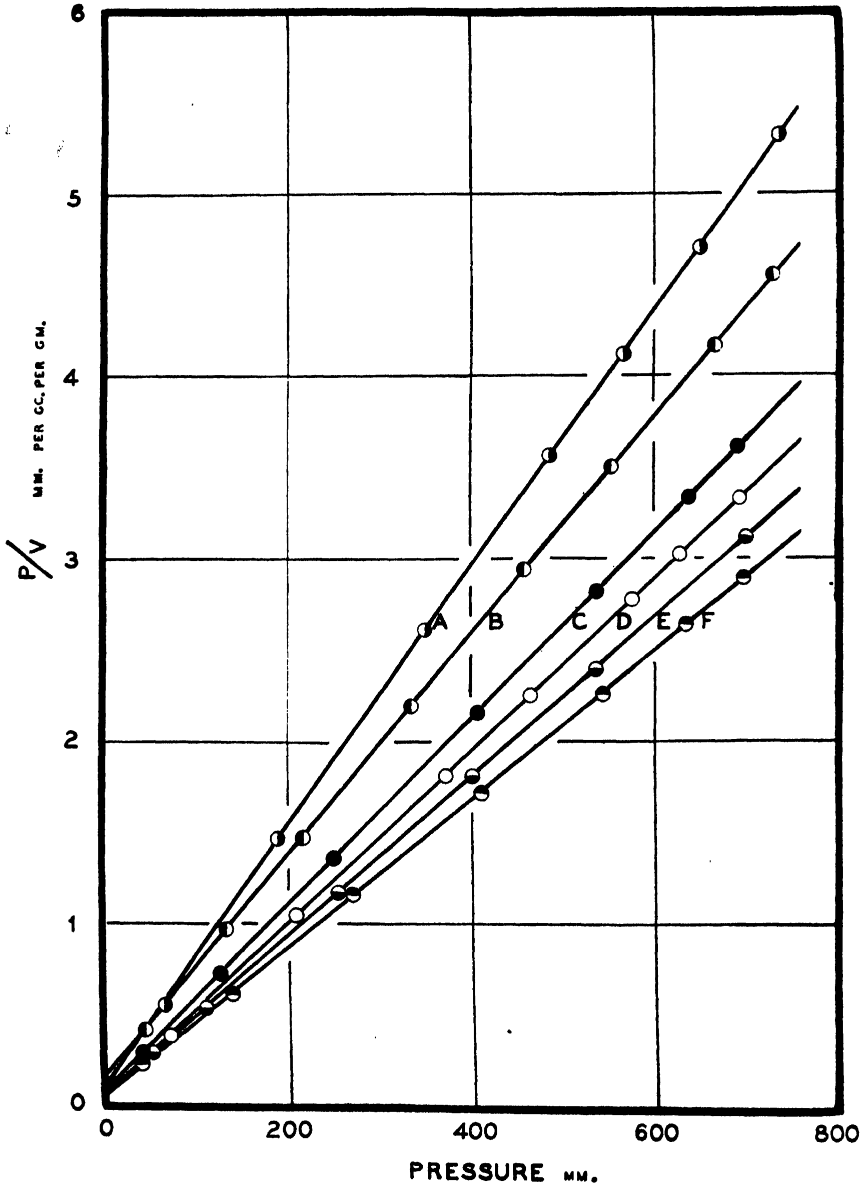

FIG. 1. *Langmuir plot for nitrogen isotherms.*

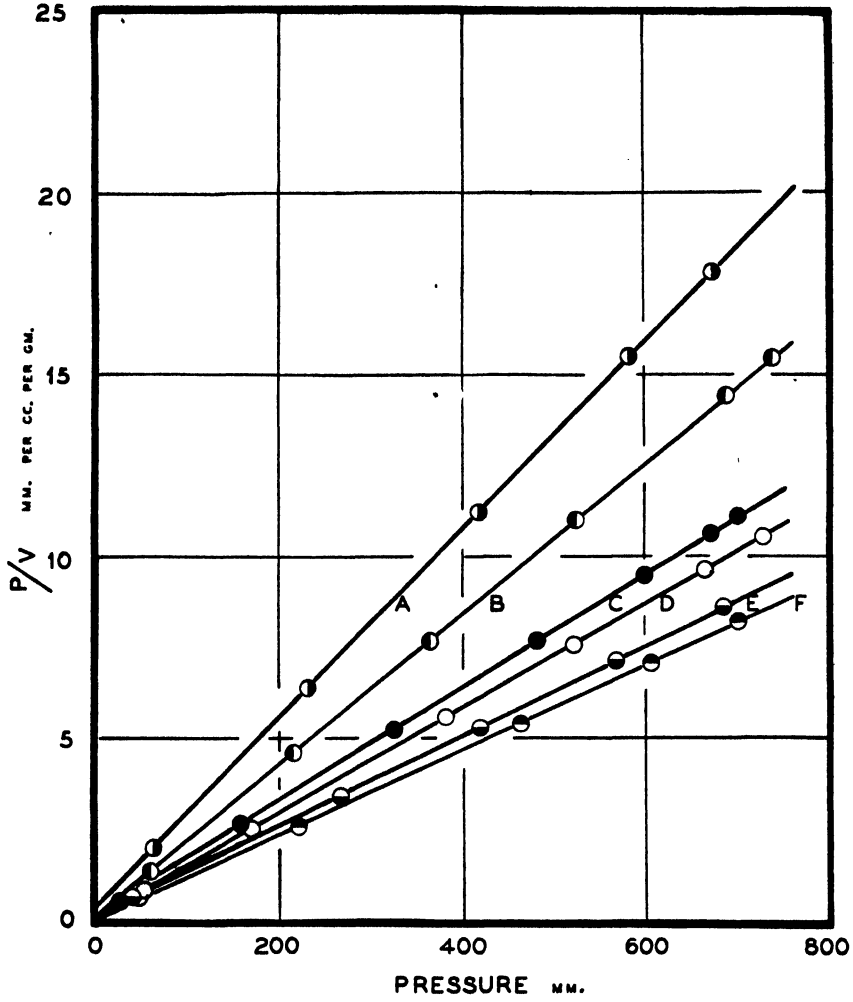

FIG. 2. *Langmuir plot for butane isotherms.*

obtained using butane are given in Table III. It is clear from these results that certain portions of the surface that are available to the nitrogen molecule are not available to the butane molecule in the less highly activated members of the series. Moreover, if the correct area for the butane molecule is 32.1 sq. Å this statement applies to all members of the cocoanut shell series. Such an explanation of the results seems indicated, since the calculated energy of adsorption remains virtually constant for both adsorbates throughout the series. From the dependence of the amount of adsorption on the size of the adsorbate molecule, one is led to expect a mean pore radius for these samples of the order of molecular dimensions.

Pore Volumes and Mean Pore Radii

The values of the density in helium and in mercury are given in Table IV. From the reciprocals of these values, the total pore volume of each sample is calculated and included in the table. It is assumed in making this calculation that the helium molecule is sufficiently small to penetrate the entire structure and that mercury does not penetrate the structure to an appreciable extent.

TABLE III

APPARENT STERIC FACTOR

Sample	Ratio of areas $\frac{\text{nitrogen}}{\text{butane}}$	
	Butane area (*a*)	Butane area (*b*)
A	1.9_3	1.2_9
B	1.7_9	1.2_0
C	1.6_2	1.0_8
D	1.6_0	1.0_6
E	1.5_2	1.0_2
F	1.5_4	1.0_3

TABLE IV

DIRECT PORE VOLUME DATA

Sample	Charcoal density, gm./cc.		Pore volume, cc./gm.
	Helium	Mercury	
A	1.98	1.09_9	0.41
B	2.01_5	1.08_5	0.42
C	2.02_2	1.01_8	0.49
D	2.03_7	0.97_4	0.54
E	2.05	0.95_4	0.56
F	2.07	0.89_1	0.64
G	1.96	0.53_5	1.33

It will be observed that a marked increase in the pore volume is brought about by the activation process. In the same way a very large increase in the surface area was shown by the data in Tables I and II. If now the voids of the particles are assumed to approximate cylinders in their form, a value of the mean pore radius may be calculated from a knowledge of the pore volume and the surface area, using the relation

$$V/A = r/2$$

where V is the pore volume per gm.

A is the surface area per gm.

r is the mean pore radius.

These values are given in Table V. Both molecular areas for the butane molecule have again been employed. It is interesting to note that the mean radius calculated from the nitrogen area is approximately constant for the cocoanut shell carbons, and somewhat larger for the zinc chloride activated sample (*G*). The larger value of the mean pore radius for this sample would be anticipated from the water adsorption isotherm, since the relative pressure at which one-half of the moisture saturation value has been adsorbed is greater than for the cocoanut shell carbons (22). The value for the cocoanut shell series is about 11 Å.

TABLE V

PORE RADII DATA

Sample	Radius in Å using $r = 2V/A$		
	Nitrogen area	Butane area (*a*)	Butane area (*b*)
A	12.7	24.6	16.4
B	11.2	20.1	13.4
C	11.0	17.7	11.8
D	11.2	17.9	12.0
E	10.5	16.0	10.7
F	11.2	17.4	11.6
G	14.8	—	—

Water Adsorption Data

The adsorption isotherms for five of the cocoanut shell samples are represented in Fig. 3. Pertinent data from these isotherms are given in Table VI. The relative pressure of water vapour at which one-half of the saturation value of moisture content has been adsorbed is given for each sample. The mean

TABLE VI

WATER ADSORPTION DATA

Sample	Relative pressure at 50% moisture saturation value	Pore radius by Cohan eqn., Å	Max. wt. adsorbed, gm./gm.	Pore volume by H_2O adsorption, cc./gm.	Ratio of pore volume filled by H_2O at saturation to total pore volume
A	0.51	8.0	0.20_8	0.20_8	0.50
B	0.51	8.3	0.22_0	0.22_0	0.52
C	0.54	8.7	0.31_5	0.31_5	0.64
E	0.57	9.5	0.37_0	0.37_0	0.66
F	0.59	10.0	0.44_1	0.44_1	0.69
G	0.72	16.2	0.93_5	0.93_5	0.70

pore radius calculated from this pressure by means of the Cohan equation (wetting angle assumed to be zero) is also given. The good agreement between the mean radius estimated by this method and that given previously is striking. It must be considered as partially fortuitous, however, in view of the direct evidence that only about 60% of the total pore volume is filled by water. This is illustrated in the last column of the table, where the volume filled by water is compared with the total volume. In making this comparison it has

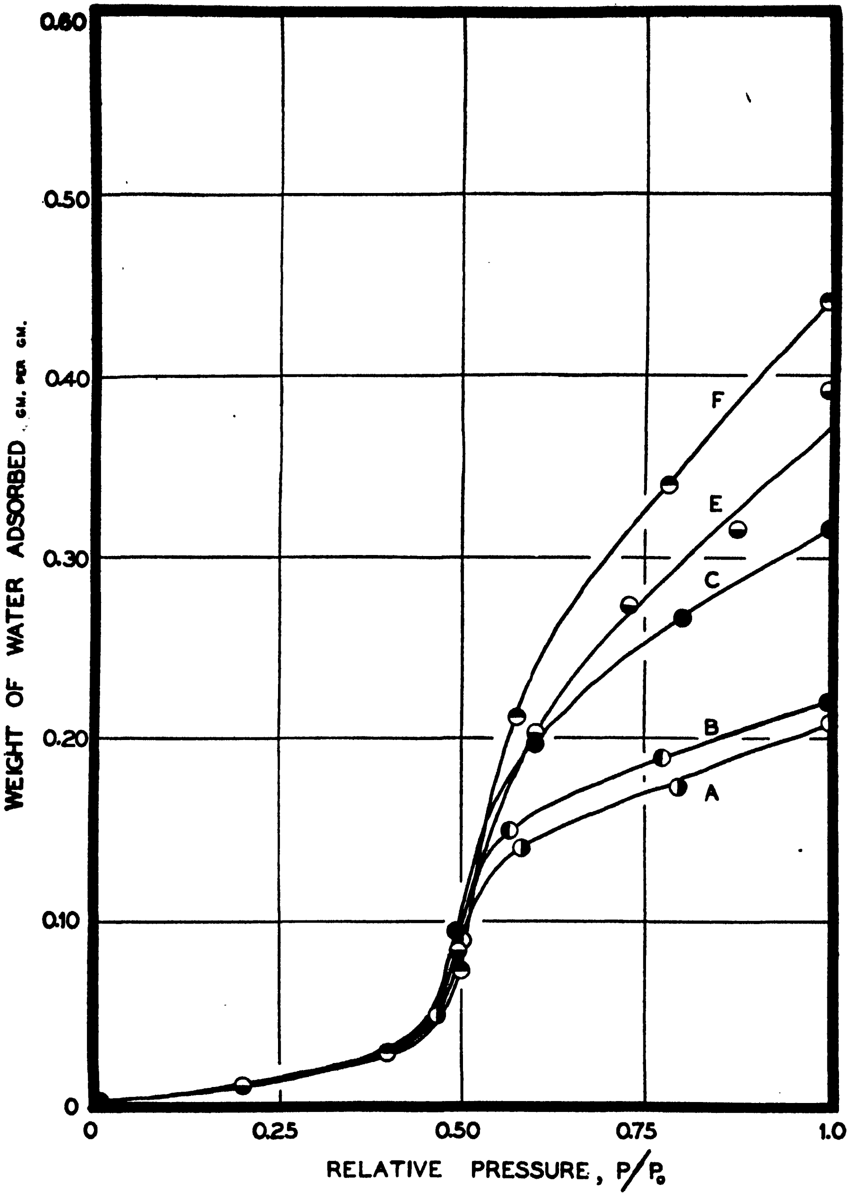

FIG. 3. *Water sorption on charcoal at 20.0° C.*

been assumed that the density of the adsorbed water may be taken as unity without serious error. This assumption has now been verified (22). Further, the value of the wetting angle has been assumed to be zero, which is apparently not justified by the form of the isotherm near saturation. Use of the Kelvin equation doubles the calculated mean pore radius.

In Table VII the area wetted by water is compared with the area determined by the Brunauer, Emmett, Teller method using nitrogen. The evalua-

TABLE VII

SURFACE AREA DATA FROM WATER ADSORPTION ISOTHERMS

Sample	Area, sq. m./gm.			Ratio $\frac{\text{water}}{\text{nitrogen}}$
	Nitrogen	Water	Free	
A	64_5	50_8	13_7	$78._8$
B	74_9	55_4	19_5	$74._0$
C	89_5	69_6	19_9	$77._8$
E	107_1	74_8	32_3	$70._0$
F	113_6	84_0	29_6	$74._0$

tion of the area wetted by water required the assumption of cylindrical voids and a zero wetting angle. With these assumptions the area may be evaluated by integration of the equation

$$A = 2\int_{w \text{ at } P}^{w \text{ at } P_0} \frac{RT \,.\, \ln \frac{P_0}{P}}{\bar{v} \,.\, \sigma} \cdot dw$$

(where w is weight of water adsorbed at a given vapour pressure) in a manner similar to that suggested by Kistler, Fischer, and Freeman (18) except that no correction has been applied for monomolecular adsorption. From the form of the isotherm it is apparent that little error can be introduced by this omission. Had the desorption isotherms been determined, an evaluation of the area by their method could have been made without assumptions as to the structure of the internal voids. Since this method applies strictly only to the desorption isotherm, the assumption of cylindrical voids and use of the Cohan equation were required with our data.

Nitrogen Adsorption on Moist Carbons

In Tables VIII and IX preliminary data on the surface areas of partially wetted carbons are given. Fig. 4 illustrates certain of the isotherms obtained from such systems. The Langmuir type of adsorption curve is again found.

The deductions from these determinations are given in the general discussion.

TABLE VIII

AREA OF WET CHARCOAL AVAILABLE TO NITROGEN AT 90.1° K

Sample *F*

Rel. press. water vap., P/P_0	Weight water adsorbed, gm./gm.	v_m, cc./gm.	$(E_1 - E_L)$	E_1	Specific surface, sq. m./gm.	Percent of total surface
			Kcal./mole			
0.0	0.0	24_7	0.9_1	2.2_4	113_6	100.0
0.47	0.05	22_4	0.9_3	2.2_6	103_0	90.6
0.87	0.38	$14._5$	1.0_4	2.3_7	6_6	5.9

TABLE IX

NITROGEN ADSORPTION DATA AT 77.3° K.

Sample	Water content	n*	v_m, cc./gm.	Surface area, sq.m./gm.	c**	$(E_1 - E_L)$	E_1
						Kcal./mole	
F	Dry	1.0	26_9	118_0	$94._2$	0.7_0	2.0_4
G	Dry	1.8	42_0	184_1	23_9	0.8_5	2.1_8
G	Sat'd	2.0	$32._4$	14_2	30_9	0.8_9	2.2_2

* *n is number of adsorbed layers.*

** $\ln c - \frac{(E_1 - E_L)}{RT}$

Discussion

The chief points of interest in the preceding data are: (1) the agreement between the mean pore radius determined by the two methods; and (2) the evidence that shows that only part of the internal volume of the carbon is utilized in the adsorption of water vapour.

The voids of an adsorbent are frequently classified according to their apparent sizes as submicro pores, micro pores, and macro pores (5, pp. 374–377). By employing the data already presented, and by considering the values of the density of each sample when immersed in water, an attempt may be made to determine the role played in the adsorption of water vapour by these three ranges of pore size.

From the pore volume filled by water vapour at saturation and from the pore volume measured directly, it is apparent that a large number of the voids do not fill with water vapour even at saturation. If the density of the carbons when immersed in water is also considered, a very small volume of approximately 0.05 cc. per gm. is seen to be unoccupied by water even under these conditions of complete immersion and one atmosphere pressure on the liquid. These voids into which liquid water will not penetrate are considered to be the submicro pores, and from the relative pressure at which adsorption of water vapour begins we are led to conclude that the submicro pores are of radius less than 6 Å. They represent only about 10% of the total pore volume, but because of their narrow radius will have a relatively large surface compared with larger pores.

It is clear also that since the volume filled by water at saturation plus the volume of the submicro pores does not equal the total pore volume, some larger pores remain unfilled up to relative vapour pressures very close to one. This is to be expected from the form of the adsorption curve near saturation, and from the finding that, even after the equilibrium saturation value of moisture content has been attained, a capacity to adsorb other vapours still exists. This residual unfilled volume is considered to be that due to the macro pores, and as may be seen from the figures in Table X is about 30% of the total pore volume. Because of the relatively large diameter of these voids they are of lesser importance in terms of area than the smaller ones.

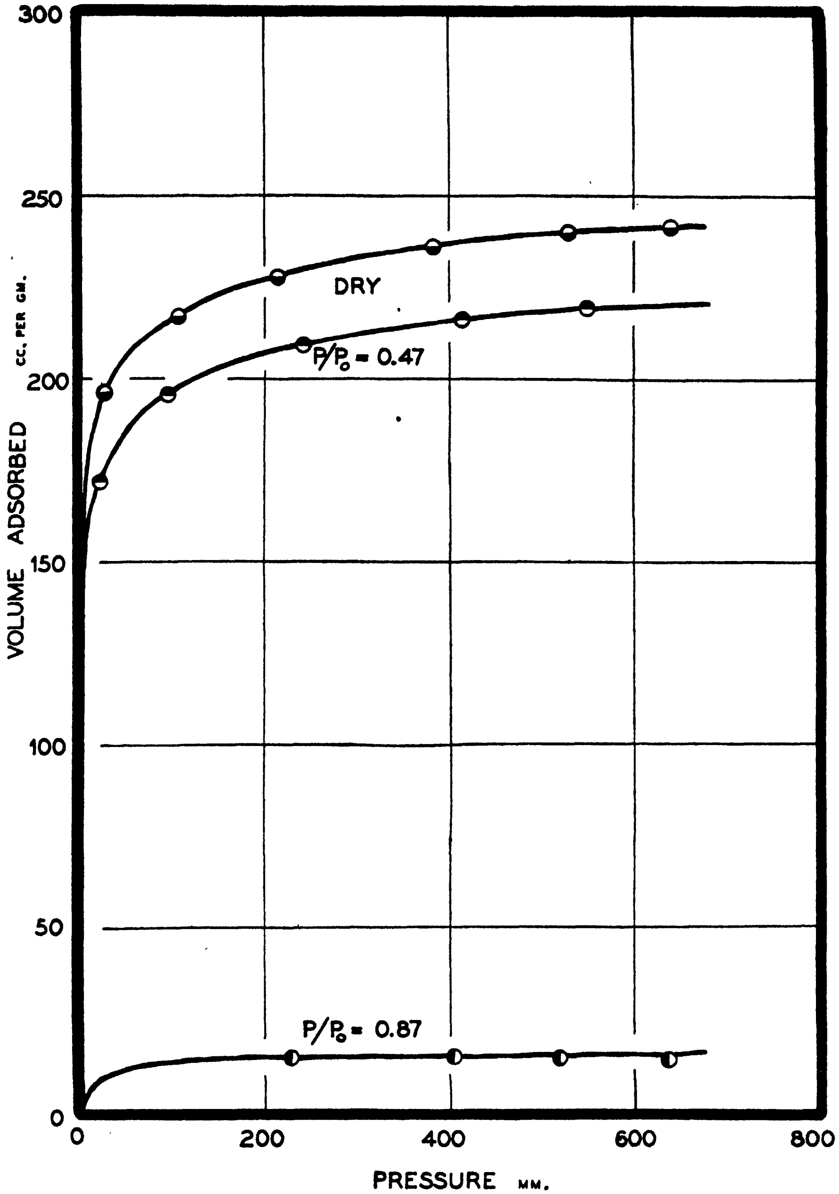

FIG. 4. *Nitrogen adsorption on Sample F in equilibrium with water vapour at 90.1° K.*

A semiquantitative check of these statements may be made with the data of Table VIII for Sample *F*. The total surface area of the dry carbon was measured as 1136 sq. m. per gm. After equilibrium had been established between the sample and a solution of 0.87 relative pressure of water vapour, the residual surface area available to nitrogen was determined and was found to be 66 sq. m. per gm. If the submicro pore volume is blocked off by the water adsorption (22), then the 66 sq. m. per gm. is the surface area of the

TABLE X

FREE VOLUMES

Sample	Density, gm./cc.		Sub-micro vol., cc./gm.	Direct pore vol., cc./gm.	Water at sat'n., gm./gm.	Free vol. at sat'n., cc./gm.		Water at 0.87, gm./gm.	Free vol. at 0.87, cc./gm.	
	H_2O	He				Total	Macro		Total	Macro
A	1.82	1.98	0.05	0.41	0.21	0.20	0.15	0.19	0.22	0.17
B	1.84_6	2.01_5	0.04	0.42	0.22	0.20	0.15	0.20	0.22	0.17
C	1.85_9	2.02	0.04	0.49	0.31	0.18	0.14	0.28	0.21	0.17
E	1.86_2	2.05	0.05	0.56	0.37	0.19	0.14	0.32	0.24	0.19
F	1.86_3	2.07	0.06	0.64	0.44	0.20	0.15	0.38	0.26	0.21
G	1.71	1.96	0.08	1.33	0.94	0.39	0.31	—	—	—

macro pores that are not filled at a relative pressure of 0.87. From Table X the volume of the macro pores is seen to be 0.21 cc. per gm. By application of the Cohan equation, the smallest pore radius into which water vapour will not condense at this relative pressure is 38 Å. The surface area associated with these larger pores may be calculated on the assumption that all are of this radius. This is not strictly correct, of course, since some will undoubtedly be larger in radius with consequent reduction of the area value. The calculated area, assuming cylinders as an approximation, is $A = 2V/r = 110$ sq. m. per gm. as compared with 66 sq. m. per gm. by experiment.

By a similar process the mean radius of the submicro pores may be estimated. Of the original surface (1136 sq. m. per gm.) about 58%, or 660 sq. m. per gm., is wetted by water at the relative pressure of 0.87. Experiment has shown that the area of the macro pores is 66 sq. m. per gm., leaving about 410 sq. m. per gm. as the area associated with the submicro pores, whose volume is 0.06 cc. per gm. The mean radius of these pores is given by $r = 2V/A = 3.0$ Å approximately. Sufficient data for other samples have not yet been obtained to test these calculations further. The agreement is extremely good, however, when one considers the numerous assumptions made, concerning the form of the voids, in the theory of the surface area measurements and in the capillary condensation theory calculations.

Conclusions

It appears that fair agreement concerning the mean pore size of an adsorbent such as activated charcoal may be obtained when these estimates are based upon either the capillary condensation theory or measurement of the total area and volume of the pores. It is also apparent that only the micro pores of the carbon are involved in the adsorption of water vapour. The submicro pores are inactive for reasons not yet clarified, while the macro pores, although readily wetted when immersed in water, do not adsorb the vapour even near saturation pressure. An estimate of the radius of the submicro pores may be made by application of the Cohan equation or by a knowledge of their volume and associated area. The same may be done for the macro pores, provided that measurements of area available to nitrogen on partially wetted carbons are made. Finally, to assess the behaviour of the carbon, a knowledge of pore volume, density in water, surface area, and the adsorption isotherm for water vapour are all required.

Acknowledgment

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THE PORE STRUCTURE AND ADSORPTIVE PROPERTIES OF SOME ACTIVATED CHARCOALS

II. THE APPARENT DENSITY OF CHARCOAL IN LIQUID MEDIA[1]

By R. M. Guest[2], R. McIntosh[3], and A. P. Stuart[2]

Abstract

The apparent density of eight charcoal samples has been determined in a series of liquids at two temperatures, 25° and 55° C. From the data a correlation between apparent density of the charcoal and surface tension of the measuring fluid is suggested. An attempt is made to explain this approximate regularity in terms of the surface free energy change on immersion.

It has been demonstrated by several investigators that the apparent density of activated charcoal or silica gel depends upon the displacement medium in which the measurement is made (7, 8, 9, 13). The causes of this are, however, still not clearly established. Recently Brunauer (5) has reviewed both the experimental evidence and the explanations that have been advanced. Cude and Hulett (7) have suggested that the differences of density may be attributed to the proportion of the total internal volume of the porous material that is filled. This view is supported by the fact that the density measured in helium is always greater than that observed in any other fluid (14). If helium is not adsorbed to an appreciable extent at the temperature of the experiment, the density in helium must be the true density, and the lower values exhibited in other media are then due to incomplete penetration into the porous structure.

Harkins and Ewing (13), noting that the greater densities were obtained in liquids of large compressibility, suggested that compression of the liquid film at the solid–liquid interface could account for the large apparent densities. They rejected the explanation of penetration since no correlation was apparent between the measured density and the ratio of the surface tension to the viscosity of the liquid. Since, for an equilibrium measurement, the viscosity of the liquid could hardly be involved, the lack of a correlation is not relevant. Moreover, the very large compressional forces (of 10,000 atm. and greater) calculated from this theory tend to discredit such an explanation as does the deduced value 1.6 gm. per cc. for the true density of activated carbon.

Culbertson and his collaborators (8, 9) have recently extended the experimental data by comparing the behaviour of charcoal and silica. They have reported, for example, that silica has a higher density in water than has charcoal, while in petroleum ether silica has the lower density. From such evidence

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Contribution from the Chemistry Department, McGill University, Montreal, P.Q.

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they have concluded that both the extent of penetration and the amount of compression may be involved, and that the forces between the solid surface and the liquid cannot be neglected.

Culbertson and Weber (9) have pursued the study further and have corroborated in the case of charcoal the apparent dependence of density on the compressibility of the fluid as first noted by Harkins and Ewing (13). This regularity did not hold for silica, however, and other factors such as dipole moments were examined in an attempt to explain the differences.

A different basis of correlation is suggested here. It has been attempted since no explanation had been advanced to account for differing degrees of penetration into the porous structures, even if that factor alone were the cause of the varying density values. Two possible reasons for a variation in degree of penetration come to mind. First, the size of some of the internal voids may be too small to permit the entrance of certain liquids. Emmett and his associates (10) have clearly established that this factor is of real importance in adsorption, and that the size of the adsorbate molecules influences the value of the surface area of the adsorbent when measured by physical adsorption. As an extreme case may be cited the behaviour of certain forms of chabasite which do not adsorb large molecules, but which have an appreciable capacity to adsorb substances whose molecules are small. Since with activated charcoal the mean pore radius is relatively small (11, 16) (of the order of 15 Å for the materials studied here), it is probable that molecular size may be of importance.

Another factor may also be operative. The free energy change on "immersional wetting" is usually considered as $\sigma_{sv} - \sigma_{sl}$, where σ_{sv} is the surface free energy of the solid–vapour interface and σ_{sl} the surface free energy of the solid–liquid interface (4). If, on immersion, conditions are such that a large change in area of the liquid–vapour interface occurs, "immersional wetting" becomes similar to "spreading wetting", and σ_{lv}, the surface free energy of the liquid–vapour interface, may be of paramount importance. Marked extension of the liquid–vapour interface will occur on immersing porous bodies, provided that the contact angle of solid–liquid is not zero. Only when this angle is zero does the free energy change

$$-\Delta F_s = \sigma_{lv}(\cos\theta - 1),$$

(where θ is the angle of contact between solid and liquid) permit spontaneous wetting. That the wetting angle between charcoal and many liquids is not zero is suggested by the form of the adsorption isotherm at saturation pressures, since the isotherm does not become asymptotic to the weight axis as a relative pressure of one is approached (12, p. 220). It follows therefore that work must be done on the system to bring about complete wetting, and, since very large surface areas are involved when dealing with activated charcoal, it is suggested that both the surface tension of the liquid and the wetting angle determine the degree of penetration when the wetting angle is not zero. Unfortunately, the determination of the wetting angle does not appear feasible and an attempt to correlate density values with σ_{lv} only has been possible.

In order to examine whether such factors as molecular size and surface free energy of liquid–vapour were influential in determining the density of charcoal, eight samples were studied in a variety of liquids. The liquids were chosen primarily because of their surface tensions, and variations of the constituent atoms or their arrangement in a regular manner was not attempted. The charcoals were chosen in the hope that a wide range of the ratio of internal volume to area would be exhibited, and thus a critical test of the compressibility theory might be attempted. However, the determination of the volume and area values, which was carried out concurrently, revealed that their ratio did not change materially.

Circumstances prevented the accumulation of similar data on several samples of silica gel, although measurements of the same type as with charcoal were begun, and no comparison of the two substances using the techniques described below is available.

Experimental

A. Charcoal

The charcoal samples consisted of seven materials made from cocoanut shell carbon and one zinc chloride activated material. The cocoanut shell carbons were obtained from the Standard Chemicals Co. Ltd., Montreal, and consisted of one series of six samples removed from the activator at approximate intervals of 24 hr., and one fully activated sample. These materials therefore represent products from a common source and common activation process, but of varying adsorptive capacity. The zinc chloride activated material, obtained through the courtesy of the National Carbon Company, was chosen in the hope that it would possess a relatively large volume-to-area ratio.

B. Pore Volume and Surface Area Measurements

The total pore volume of each sample was measured by determining its density in helium and in mercury (11). The apparatus and method used in finding the helium density were essentially the same as those reported by Howard and Hulett (14) and have already been sufficiently described (11). The assembly in which the density in mercury was found has also been reported in the earlier publication (11). The measurements of surface area were made using the method of Brunauer, Emmett, and Teller (6) employing nitrogen at liquid air temperature, and the values have already been reported (11).

C. Determination of the Density in Various Liquids

The pycnometer used to measure the densities in the liquids was of the following design. A piece of 15 mm. Pyrex tubing was sealed to an ordinary type of pycnometer just below the ground glass opening of the pycnometer. A side-arm was then sealed to this connecting tube, and a constriction made in the side-arm, which was bent as shown in Fig. 1, to facilitate its immersion in the liquid. A fragile tip was made on the side-arm. The charcoal sample was placed in the pycnometer bulb and the whole assembly sealed to an evacuating system through the 15 mm. Pyrex tube. About eight such assemblies were then surrounded by an air-bath maintained at 110 ± 5° C. and the charcoal thoroughly evacuated at this temperature. When the pressure over the charcoal had fallen to between 10^{-4} and 10^{-5} mm. of mercury at 110° C., the connecting tubes were carefully sealed off, with the pumps operating. The pycnometer bulb, connecting tube, and charcoal were then weighed. The tip of the side-arm was next broken under the surface of the liquid, and the charcoal wetted. Next, the connecting tube was broken at the approximate position of the dotted line of Fig. 1, and the pycnometer capillary inserted in the ground glass neck.

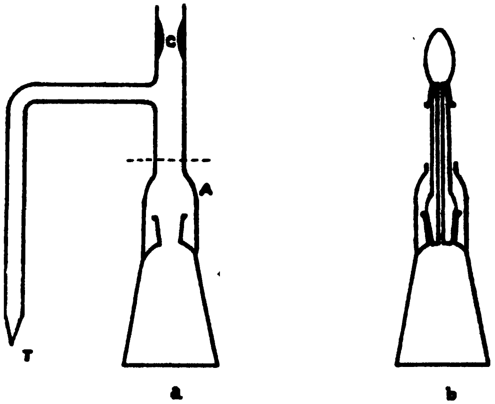

FIG. 1. *Pycnometer for measuring apparent density of charcoals.*

The only difficulty encountered when using this type of pycnometer was in freeing the space between the connecting tube and the pycnometer neck of liquid. This was achieved by blowing the space out thoroughly with dried air.

D. Purification of Wetting Liquids

The liquids employed were reagent grade materials, except the nitrobenzene, which was purified by fractional crystallization, followed by vacuum distillation. Ordinary distilled water was employed in making determinations with water. All liquids were degassed by boiling under reduced pressure just before use. Non-aqueous materials were kept dry by storage over Drierite. When making measurements with glycerine and with ethylene glycol the pycnometers were placed in closed containers with Drierite present, and the containers then placed in the thermostats.

E. Establishment of Equilibrium Values

In order to ensure that the determined density values should be as free as possible from errors, the time required to establish a constant density value was first investigated. Benzene, ethyl acetate, and pyridine were used in this test, and the weights of the pycnometers containing charcoal and these liquids followed until no further changes were observed. The pycnometers were then taken from the thermostat operating at 25 ± 0.01° C., and placed in a thermostat operating at 55 ± 0.01° C., and changes were again followed until they became negligible. The vessels were then replaced in the 25° C. bath and again examined. This procedure was repeated until the density value obtained at either temperature was constant. Typical data are given for ethyl acetate in Table I, and are represented for the three substances in Fig. 2.

TABLE I

Variation of apparent density with time

Time, days	Pycnometer (bottom) charcoal + ethyl acetate, gm.	Temperature, °C.	Density, gm./cc.
1	85.825	25	2.05
2	85.852		2.06
4	85.868		2.06_9
5	85.872		
6	85.874		
7	85.875		2.07_2
10	84.563	55	
11	84.564		
12	84.566		2.09_4
14	84.578		
15	84.583		2.10_1
16	84.586		
20	84.588		2.10_3
21	85.909	25	
22	85.908		
23	85.908		
24	85.912		
25	85.912		2.08_8
31	84.590	55	2.10_6
34	84.593		
36	84.592		
38	84.592		
39	84.595		
40	84.595		
41	84.594		2.11
42	85.911	25	
43	85.910		
47	85.915		
48	85.914		
49	85.914		2.09
50	84.594	55	
51	84.590		2.11
52	85.916	25	
53	85.917		
54	85.914		
85	85.915		
86	85.915		2.09

It was thus established that drifts were not appreciable after 30 to 40 days, and the practice was adopted of allowing the pycnometers to stand at a given temperature for about 30 days before being weighed. If then significant changes were not observed over a period of a week (temperatures were varied if the boiling point of the liquid permitted) the values were taken as equilibrium values. From the initial rate of drift it appears doubtful whether determinations of density after two hours, as performed by Culbertson and Dunbar and Weber (8, 9), are significant where small differences in density are observed.

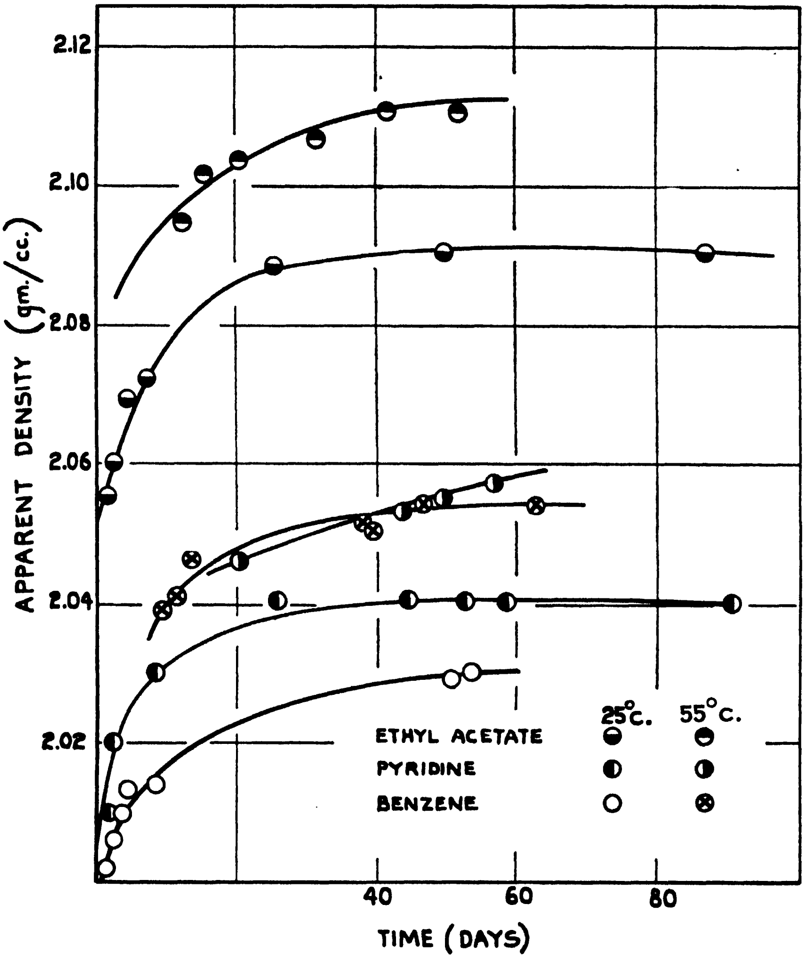

FIG. 2. *Illustration of rate of attainment of equilibrium in density determinations.*

The variation of the temperature of measurement was also useful in testing the relation between density and surface tension, and two temperatures were always employed where feasible.

F. Expansion of the Solid

The investigations of McBain, Porter, and Sessions (15) and Bangham and Razouk (3) have shown that porous adsorbents such as charcoal swell when vapours are adsorbed. Changes in volume of the adsorbent also occur when the solid is immersed in the liquid. This correction factor for the density has apparently not been applied by earlier workers, nor has it been applied in this investigation. From the data obtained in adsorption studies it appears that the expansion is small, about 0.5% at saturation pressure for methyl alcohol and is about the same order for all adsorbates. No serious error is to be expected in the general nature of the results given below owing to this omission.

Results

The complete data for the cocoanut shell sample which had been fully activated (*S.B.T.* No. 95) are given in Table II. Similar data for the zinc chloride activated sample (*C.W.S.N.* 178 *B*-2) are given in Table III. These data are also plotted against the value of the surface free energy liquid–vapour of the liquids (Figs. 3 and 4) which were chosen, as stated above, to achieve as wide a variation of this property as possible. Surface free energy values were obtained from the International Critical Tables.

TABLE II

SUMMARY OF APPARENT DENSITY DATA FOR *S.B.T.* 95

Liquid	25° C.		55° C.	
	Surface tension, dynes/cm.	Density of charcoal, gm./cc.	Surface tension, dynes/cm.	Density of charcoal, gm./cc.
Water	72.0	1.90_7	67.0	1.88_6
Glycerine	63.0	1.96_8	61.0	1.95_6
Ethylene glycol	47.0	1.94_5	44.5	1.93_5
Nitrobenzene	43.3	2.01_2	39.8	2.02
Pyridine	37.1	2.04	32.9	2.05_1
Chlorobenzene	32.5	2.04_6	29.0	2.05_3
Carbon disulfide	31.4	2.07_3		
Xylene	29.6	2.04_6	26.2	2.06_3
Benzene	28.2	2.03_1	24.4	2.05_3
Toluene	27.9	2.04_9	24.3	2.06_7
Chloroform	26.4	2.04_8		
Carbon tetrachloride	26.3	1.94_5	22.6	1.96_7
Ethyl acetate	23.3	2.09_1	19.7	2.11
Acetone	23.3	2.12		
Methyl alcohol	22.4	2.07_6	19.8	2.09_1
Ethyl ether	16.4	2.12_6		
Pentane	14.8	2.11_8		

Data obtained with the six samples of the series of cocoanut shell carbons of various periods of activation (Samples *A* to *F*) are given for 25° C. in Table IV and 55° C. in Table V. The total pore volume and the fraction of

TABLE III

SUMMARY OF APPARENT DENSITY DATA FOR *C.W.S.N.* 178 *B*-2

Liquid	25° C.		55° C.	
	Surface tension, dynes/cm.	Density of charcoal gm./cc.	Surface tension, dynes/cm.	Density of charcoal, gm./cc.
Water	72.0	1.70_9	67.0	1.68_9
Pyridine	37.1	1.86_2	32.9	1.87_4
Chlorobenzene	32.5	1.88	29.0	1.89_2
Benzene	28.2	1.84_9	24.4	1.87_6
Carbon tetrachloride	26.3	1.85_1	22.6	1.87_2
Ethyl acetate	23.3	1.88_6	19.7	1.91_3
Ethyl ether	16.4	1.93_7		

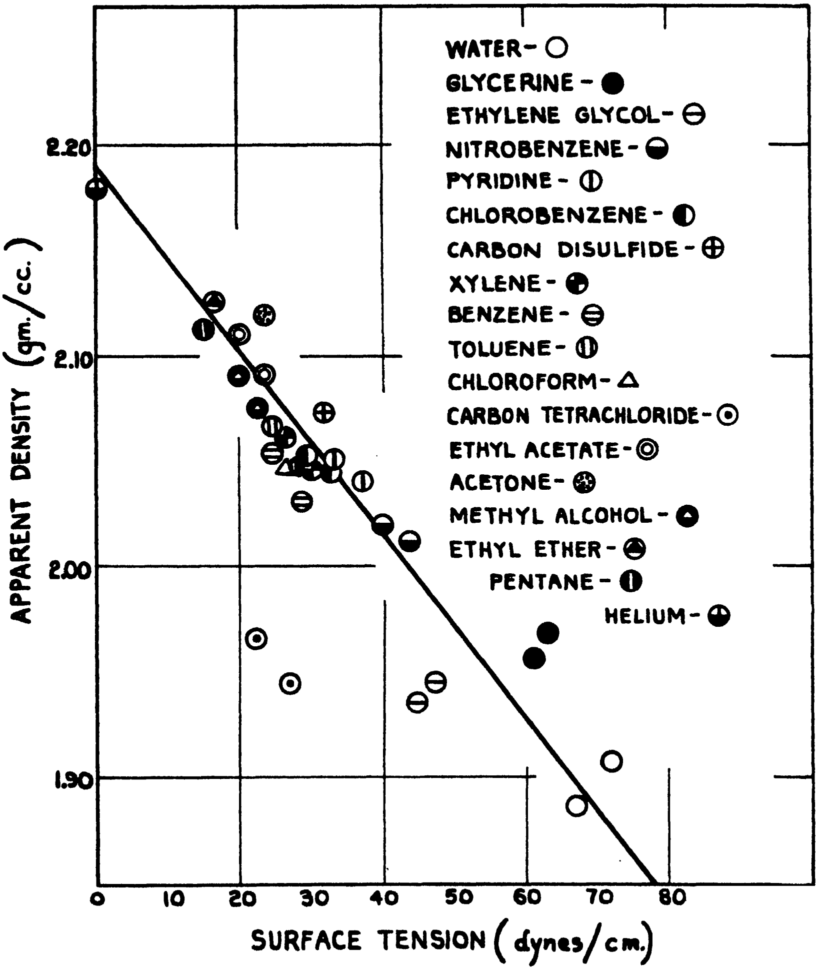

FIG. 3. *Apparent density of charcoal sample S.B.T. 95 as function of the surface tension of the liquids.*

TABLE IV

APPARENT DENSITIES OF PROGRESSIVELY ACTIVATED SAMPLES IN SEVERAL LIQUIDS AT 25° C.

S.B.T. No. 72 Density, gm./cc. *T* = 25° C.

Sample No.	Carbon tetra-chloride	Ethylene glycol	Water	Chloro-benzene	Benzene	Pyridine	Ethyl acetate
A	1.38_2	1.81_5	1.82	1.79_9	1.82_6	1.88	1.91_7
B	1.43_2	1.82	1.84_6	1.83_2	1.84_8	1.91_9	1.89_7
C	1.59_8	1.83	1.85_9	1.89_8	1.91_4	1.93_5	1.96_5
D	1.69	1.89_2	1.86_2	1.92_2	1.97_5	1.97_4	1.98_8
F	1.82_2	1.92_7	1.86_2	1.93_9	1.96_9	2.01_3	2.01_2
F	1.92_5	1.92_6	1.86_3	1.96_9	2.00_2	2.01_8	2.02_9

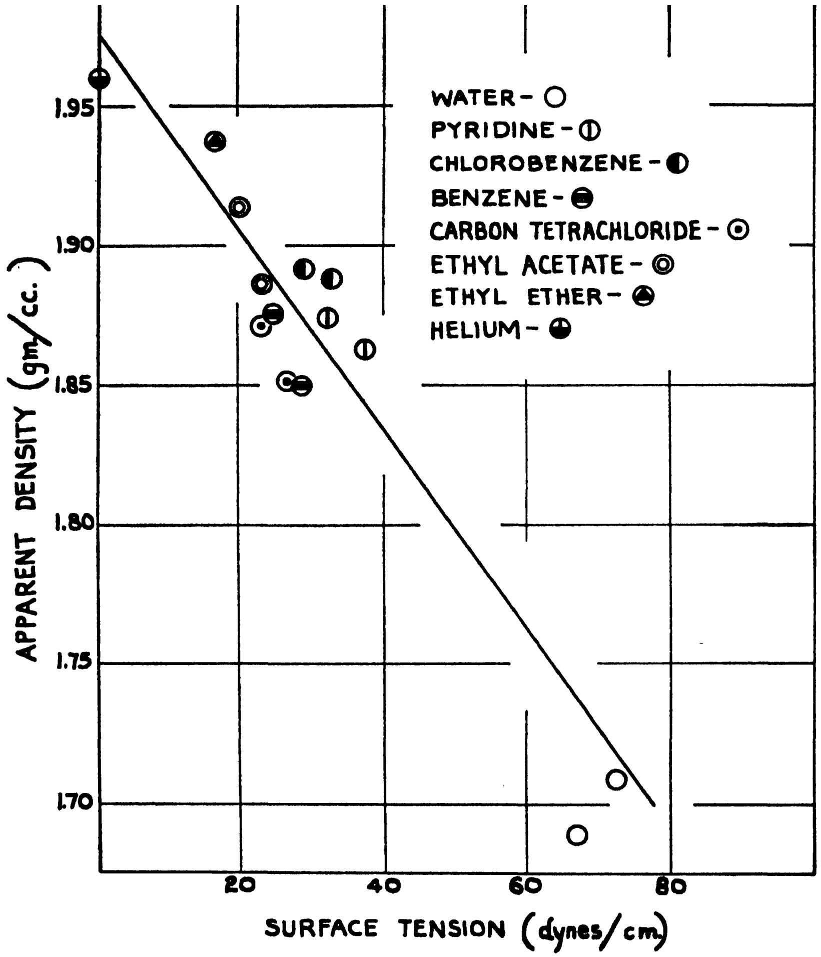

FIG. 4. *Apparent density of charcoal sample C.W.S.N. 178 B-2 as function of the surface tension of the liquids.*

TABLE V

APPARENT DENSITIES OF PROGRESSIVELY ACTIVATED SAMPLES IN SEVERAL LIQUIDS AT 55° C.

S.B.T. No. 72 Density, gm./cc. $T = 55°$ C.

Sample No.	Carbon tetra-chloride	Ethylene glycol	Water	Chloro-benzene	Benzene	Pyridine	Ethyl acetate
A	1.38_3	1.81_4	1.81	1.82_3	1.84_7	1.90	1.93_5
B	1.43_4	1.81_8	1.83_6	1.85_4	1.86_7	1.92_8	1.91_5
C	1.60_4	1.82_9	1.84_5	1.91_7	1.93	1.94_3	1.98_2
D	1.69_3	1.88_8	1.84_2	1.94_7	1.99_4	1.98_3	2.00_3
E	1.83_5	1.92_5	1.84_8	1.96_4	1.99_1	2.02_3	2.03
F	1.93_9	1.92_6	1.84_6	1.99_4	2.02_2	2.03_1	2.04_9

the total pore volume filled for each sample by the various liquids are given for the two temperatures in Tables VI and VII. Finally, the necessary values of density in helium, density in mercury, surface area, and volume-to-area ratio are given for all samples in Table VIII, although some of these values have been reported earlier (11).

TABLE VI

FRACTION OF PORE VOLUME FILLED BY LIQUID AT 25° C. FOR SAMPLES OF TABLE IV

S.B.T. No. 72

Sample No.	Total pore volume, cc./gm.	Fraction filled by:						
		Carbon tetra-chloride	Ethylene glycol	Water	Chloro-benzene	Benzene	Pyridine	Ethyl acetate
A	0.41	0.69_7	0.91_7	0.91_9	0.91	0.92	0.95	0.97
B	0.42	0.71	0.90	0.91_5	0.91	0.91_7	0.95	—
C	0.49	0.79	0.90_5	0.92	0.93_5	0.94_5	0.95_6	0.97
D	0.54	0.83	0.93	0.91	0.94	0.97	0.97	0.97_6
E	0.56	0.89	0.94	0.90_8	0.94_5	0.96	0.98	0.98
F	0.65	0.93	0.93	0.90	0.95	0.96_6	0.97	0.98

Discussion

The data of Table II for sample *S.B.T.* No. 95, which are represented in Fig. 3, indicate that as a first approximation there exists a relation between surface tension of the liquid and the apparent density. It should be noted also that the value of the density at zero surface tension, obtained by extrapolating the line through the liquid density points, agrees closely with the density value determined by use of helium. In general also, density values obtained at the higher temperature, and thus at a lower surface tension of the same liquid, are higher than the values obtained at the lower temperature. Unfortunately, the variation in surface tension of the liquid due to tem-

TABLE VII

FRACTION OF PORE VOLUME FILLED BY LIQUID AT 55° C. FOR SAMPLES OF TABLE V

S.B.T. No. 72

Sample No.	Total pore volume, cc./gm.	Fraction filled by:						
		Carbon tetra-chloride	Ethylene glycol	Water	Chloro-benzene	Benzene	Pyridine	Ethyl acetate
A	0.41	0.69_7	0.91_8	0.91	0.92	0.93	0.96	0.97_6
B	0.42	0.71	0.90	0.91	0.92	0.92_5	0.95_5	0.95
C	0.49	0.79	0.90	0.91	0.94_6	0.95	0.96	0.97_7
D	0.54	0.83	0.92_6	0.90_5	0.95_5	0.96	0.97	0.98_5
E	0.56	0.89_5	0.94	0.90	0.95_7	0.97	0.98_6	0.99
F	0.65	0.936	0.93	0.89	0.96	0.96_7	0.98	0.99

TABLE VIII

DATA REQUIRED TO EVALUATE MEAN PORE RADIUS

Sample No.	Density in mercury, gm./cc.	Density in helium, gm./cc.	Area, sq. metres/gm.	Mean pore radius, Å
S.B.T. No. 72				
A	1.09_9	1.98	644	12.7
B	1.08_5	2.01_5	792	10.6
C	1.01_8	2.02	895	10.9
D	0.97_4	2.03_7	963	11.2
E	0.95_4	2.05	1070	10.5
F	0.89_1	2.07	1136	11.3
S.B.T. 95	0.89_9	2.18	1220	10.7
C.W.S.N. 178 *B*-2	0.53_5	1.96	1840	14.8

perature is not large, and the data should be extended over a wider temperature range. Three liquids were the exceptions to this rule for all carbon samples studied. These were glycerine, ethylene glycol, and water, and all gave lower apparent density values at the higher temperature.

Although the data for sample *C.W.S.N.* 178 *B*-2 are not nearly as extensive as for the cocoanut shell sample, again in general the lower surface tension liquids yield higher density values for the carbon.

In the case of the cocoanut shell series, *S.B.T.* No. 72, it is clear that some factor other than surface tension is involved in the apparent density value. For slightly activated carbons it is seen that carbon tetrachloride, for example, may give lower density values than water, although that result would not be expected from the data on *S.B.T.* No. 95. From the tables showing the fraction of the total pore volume filled for the several liquids on this series of carbons, it is apparent that during activation some property of the carbon is being altered so that a variation in the proportion of the total volume filled is brought about.

From the standpoint of the penetration theory, the size of the internal voids might be considered as the determining factor. On this basis it would appear that the average void size must be increasing as activation proceeds. This suggestion is not supported by the independent evaluation of mean pore size made by means of the total volume and area measurements. From these latter data it appears that the mean pore radius is substantially constant throughout the series. (Sample *A* has a higher value which may be due to the inability of nitrogen to penetrate the pores, giving a low surface area value). Further, it should be noted that for water a slight decrease in the fraction of the volume filled occurs as the extent of activation is increased. These results suggest that some factor other than the average pore dimension is involved.

The theory that compressibility of the liquids accounts for density variations will not explain these observations. As the volume-to-area ratio is nearly constant, wide variations in the amount which the liquids are compressed is not to be expected, unless the nature of the surface is altered. From the values of E_1 for nitrogen, the energy of adsorption of the first layer, reported earlier (11), the nature of the surface appears unchanged and only the extent of surface appears to vary as activation is continued. Also, carbon tetrachloride or benzene would not be expected to show lower density values than are exhibited in water.

From the viewpoint outlined in the introduction, the apparent density value will depend upon the free energy change brought about on immersion in the liquids. The value of the energy change is seen to depend both upon the surface tension of the liquid–vapour interface and upon the wetting angle at the solid–liquid interface. Variations in the wetting angle for the series of increasing activity could conceivably cause the observed variations in apparent density. On this basis, however, the change in wetting angle with temperature must be negligible for all the liquids except glycerine, ethylene glycol, and water. Too little is known concerning the factors that govern the value of a wetting angle (2, 3, 17) to permit further discussion at the present. The anomalous behaviour of water should be stressed, however, in view of its peculiar adsorption isotherm on charcoal. From the results with glycerine and ethylene glycol, similarities to the adsorption isotherm of water might also be expected in the adsorption isotherms of these substances.

To recapitulate, it appears that the value of the apparent density of charcoal immersed in a given liquid will be determined primarily by the surface tension of the liquid and by the wetting angle of the solid–liquid interface. Factors such as molecular size in relation to diameter of the internal voids or the compressibility of the liquid employed do not appear to explain the results adequately.

Acknowledgment

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THE PORE STRUCTURE AND ADSORPTIVE PROPERTIES OF SOME ACTIVATED CHARCOALS

III. THE APPARENT DENSITY OF WATER ADSORBED ON ACTIVE CHARCOAL[1]

By J. A. Morrison[2] and R. McIntosh[3]

Abstract

The apparent density of water adsorbed on four different charcoals at 20° C. has been measured by a method of helium displacement. At low relative pressures the density is appreciably higher than that of liquid water, but falls rapidly to nearly the normal density as the amount adsorbed increases. A very sharp drop in density occurs close to saturation; and is attributed to the blocking of the very small porous spaces through the advent of capillary condensation in this region. It is suggested that the apparent high initial density is due to the size of the molecules of the measuring fluid rather than to the compression of the adsorbed film.

The apparent density of the adsorbed water on the desorption branch of the isotherm differs from that on the adsorption branch, which suggests that the mechanisms of adsorption and desorption differ. An attempt has been made to evaluate the constants V_m and C of the multimolecular adsorption theory from one of the adsorption isotherms.

Introduction

The greater part of information concerning adsorption processes has been derived from measurements of the adsorption isotherms and heats of adsorption of vapours on solids. All of the several theories of adsorption that have been proposed include postulations about the nature of the adsorbed film. Relatively few direct measurements of the properties of the adsorbate have been made. In what follows, the density of water adsorbed on charcoal has been determined by a method of helium displacement with a view to establishing the value of this property as a guide to the adsorption mechanism. On the basis of published data, none of the theories seems to describe water adsorption adequately.

The occurrence of limited hysteresis in the adsorption of water on charcoal has lead to speculation concerning the applicability of the capillary condensation theory. It has been shown (10) that, using the concept of Cohan (5) of adsorption in annular rings, it is possible to derive a value of the mean pore radius that is in fair agreement with that derived from the ratio of the pore volume to the surface area of the charcoal. On the basis of capillary condensation, the slope of the adsorption branch of the isotherm is attributed to a lack of homogeneity of pore sizes, and analyses of the distribution of pore sizes and number of pores have been attempted (13). However, the same distribution should be obtained from the desorption branch, provided

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only that the mechanism of desorption is different, and that no error has been made in the hypothesis. In general, for water adsorption, this criterion does not appear to be met, the desorption branch indicating a nearly homogeneous adsorbent in terms of pore size (e.g., Fig. 4).

McBain, Porter, and Sessions (14) have shown that charcoal expands when water is adsorbed, just as it does when other vapours are adsorbed. For this reason, McBain has rejected the capillary condensation theory for water adsorption. If the adsorbed water exists under menisci it should be under tension and should not expand the charcoal.

The multimolecular adsorption theory (3) treats water adsorption as a special case of multilayer formation where initially E_1, the heat of adsorption of the first layer, is less than E_L, the heat of liquefaction of the vapour. It is possible with the help of the theory to obtain an isotherm equation that fits the experimental isotherm, but there appears to be a discrepancy in the surface area values derived from it (3). The theory predicts that at the saturation pressure the capillaries are not full, a prediction verified by experiment (10).

Of several papers describing the determination of the density of adsorbed films, two are of interest here. De Vries (7) has measured the density of carbon dioxide, and Danforth and De Vries (6) the density of carbon tetrachloride and of acetone adsorbed on charcoal. In the interpretation of the results, these authors appear to have neglected the effect of the structure of the adsorbent, and the effect of the molecular size of the displaced fluid. By using several samples of charcoal whose physical properties were determined by independent measurements, an attempt has been made in the present investigation to evaluate the magnitude of these effects. It appears that they are of considerable importance.

Experimental

The method employed was similar to that of Filby and Maass (9) using the technique of gas expansion. A schematic diagram of the essential parts of the apparatus is shown in Fig. 1. The charcoal sample was contained in the bulb *D*, which could be detached from the system for weighing. The expansions with helium were made from the standard volume *C* to the cell *D*. *C* and *D* were made approximately of the same volume so that the precision was optimal. This section of the apparatus was totally immersed in a water-bath controlled to 20° ± 0.02° C., which eliminated the necessity of making temperature corrections on the expansions, and greatly improved the reproducibility of the results. Pressures were read on a constant volume mercury manometer with glass scale attached to a manifold. Connection between the manifold and the part of the apparatus in the water-bath was made through the short manometer *E*. For each pressure measurement, the level of the mercury in one arm of the short manometer was brought to the tip of a fixed glass pointer. All pressures were corrected to a reference of a mercury column at 0° C. Ground glass check valves at the top of both arms of the short manometer made it possible to evacuate either side without drawing mercury into the system.

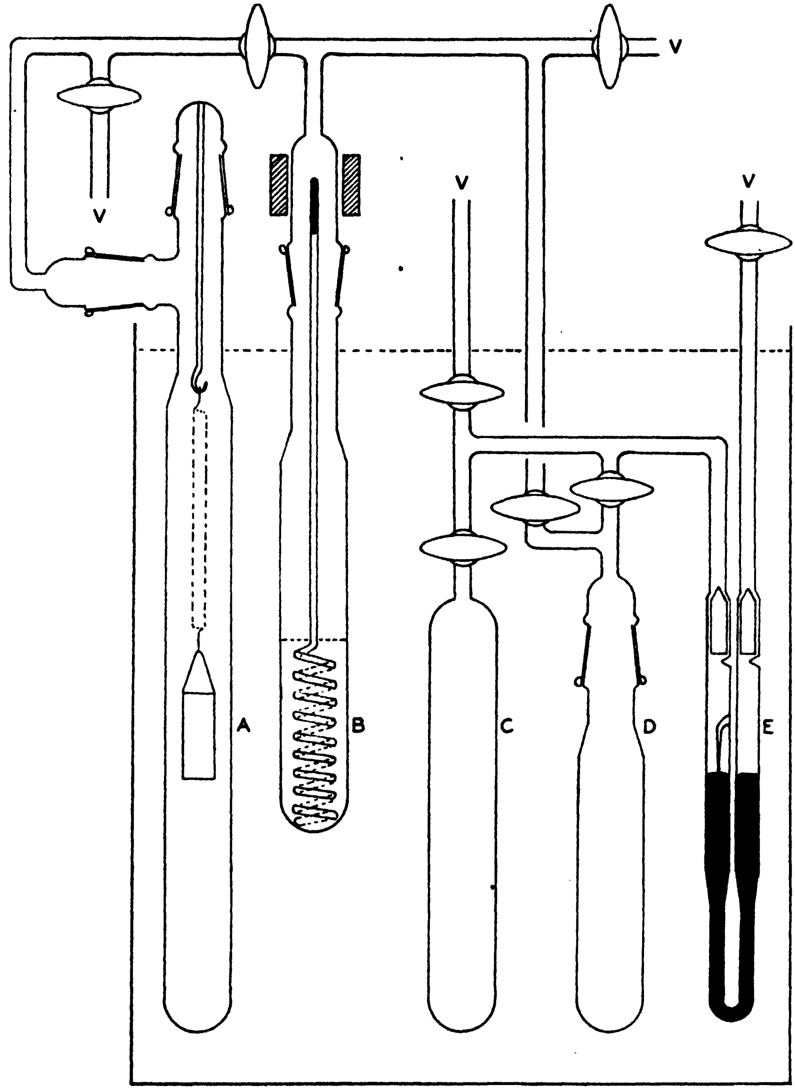

FIG. 1. *Schematic diagram of the principal parts of the apparatus.*

Connections with the manifold and vacuum system were made at *V* shown in Fig. 1. The charcoal was degassed by heating to approximately 130° C. and evacuating until a pressure of 5×10^{-5} mm. of mercury was maintained. Evacuation was performed with a two stage mercury diffusion pump, backed by a Hyvac oil pump.

To the manifold was attached the helium purification and storage system. The helium was purified by passing it slowly over degassed charcoal cooled in liquid air, and was stored in a 12 litre bulb. Just before use, it was passed again through the purification train. Any desired pressure within the system could be established with a Toepler pump. The pump was also of use in obtaining fine adjustment of the pressure in the manifold to balance that in the expansion system.

Different pressures of water vapour were developed by using solutions of sulphuric acid and water contained in *B*. The solutions were degassed thoroughly by freezing at dry ice temperatures and evacuating several times.

While water vapour was being adsorbed on the charcoal, the solution was agitated with a glass stirrer. The stirrer had a piece of soft iron sealed into the top, and was actuated by a solenoid on the outside.

A spring balance *A*, of No. 32 gauge phosphor-bronze wire, with an extension of approximately 2.7 cm./gm., was connected with the water reservoir *B* and the charcoal cell *D*, and was used to determine when the charcoal was in equilibrium with the water vapour. Approximately one gram of charcoal was contained in a basket made of copper screen, which was hung at the lower end of the spiral. The extension of the spiral was followed with a cathetometer.

Operation

After the charcoal had been degassed, the free volume in the cell *D* was determined by expanding helium from the calibrated volume *C* into *D*. The final pressure was followed for approximately eighteen hours. Slight drifts in pressure were sometimes observed immediately after the expansion, but these were attributed to the establishment of temperature equilibrium. No drifts extending over a period of hours such as reported by Howard and Hulett (12) were ever observed.

At least 48 hr. was allowed for the charcoal to come to equilibrium with the water vapour from *B*, and the free volume in the cell *D* was again determined. However, in this case the expansion was performed with a mixture of water vapour and helium. Before the expansion, *C* was filled with water vapour at the same pressure as in *D*, and an appropriate amount of helium was added quickly. When the pressure had become constant, the gas was expanded into *D*, and 18 to 24 hr. was allowed for equilibrium to be established. The free volume was calculated on the basis of the partial pressure of helium, which was obtained by subtracting the partial pressure of water vapour from the total pressure. That this procedure is permissible was shown by the determination of the volume of a glass bulb by expansion with several mixtures of helium and water vapour. Volumes so determined agreed within 0.05% with the volume as found by expanding dry helium. The volume of water adsorbed on the charcoal was determined then by the difference between the initial and final free volumes. The weight of water was found by detaching *D* from the apparatus and weighing. In this operation the pressure of helium in *D* was brought up to atmospheric and the cell was stoppered firmly as soon as it was detached. Altogether, a period of from seven to nine days was required for a single determination.

It is difficult to assign a value for the accuracy of the determinations owing to the possibility that the adsorbed film may not build up in the same manner in successive determinations. On the basis of the results, it appears that the precision of the measurements is about 1% at saturation and about 3% at the lowest pressures used. Unless the solubility of helium in the adsorbed film is considerably greater than in liquid water, no appreciable error is introduced by neglecting this factor. Expansion of the charcoal particles when water is adsorbed (14) is also insufficient in magnitude to introduce errors.

Charcoals

In Table I are given data that describe some properties of the charcoals that were used. Charcoal *D* was prepared by leaching charcoal *C* for 24 hr. with 50% aqueous hydrofluoric acid. The charcoal was then washed thoroughly with distilled water and dried. The densities of the charcoals in helium, in water, and in mercury were measured at 20° C. The densities in water were determined by Major J. C. Arnell of the Chemical Warfare Laboratories, Ottawa. The surface areas were measured by nitrogen adsorption at −183° C. after the method of Brunauer, Emmett, and Teller (4).

TABLE I

A SUMMARY OF THE KNOWN PROPERTIES AND PREPARATIONS OF THE CHARCOAL SAMPLES

Charcoal	*A*	*B*	*C*	*D*
Manufacturer	National Carbon	Standard Barneby	National Carbon	National Carbon
Designation	*CWSN* 178*B*-2	Charge 72	*CWSN* 212*A*-1*X*	*CWSN* 212*A*-1*X*
Starting material	Wood	Cocoanut shell	Wood	Wood
Activation	Zinc chloride	Steam	Zinc chloride	Zinc chloride
Density in helium	1.91	2.07	2.11	2.09
Density in water	1.74	1.86	1.86	1.83
Density in mercury	0.54	0.89	0.66	—
Ash content, %	1.6	0.5	4.0	0.7
Surface area, m.^{2}/gm.	1840	1140	—	—

Results

The results of the measurements of the density of water adsorbed on the four charcoals are recorded in Tables II to VI, and are plotted in Figs. 2 and 3. To bring the curves to the same relative basis, the apparent density is plotted against the percentage of the adsorption at saturation for each charcoal. Data in Tables II to V pertain to measurements on the adsorption branch of the isotherms, while those in Table VI refer to measurements on the desorption branch for charcoal *D*.

It is at once apparent that the plots in Figs. 2 and 3 are of similar form, characterized by high density at small amounts adsorbed, followed by a rapid

TABLE II

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL *A* (33.27 GM.)

Run No.	Time to eq. with water vapour, hr.	p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
2	48	1.00	171.27	32.65	31.16	0.95_4	0.937	100
3	101	0.74	185.55	18.37	18.86	1.02_7	0.567	60.3
4	120	0.74	183.42	20.50	20.78	1.01_4	0.625	66.4
5	81	0.59	199.48	4.44	5.18	1.16_6	0.156	16.6
6	56	0.59	199.74	4.18	4.86	1.16_2	0.146	15.6
7	51	0.67	194.22	9.70	9.89	1.02_0	0.297	31.6
8	80	0.66	194.69	9.23	9.70	1.05_1	0.292	31.1
9	80	0.87	175.13	28.79	29.41	1.02_1	0.884	94.2
10	77	0.91	174.39	29.53	30.04	1.01_7	0.903	96.0
11	72	0.97	173.27	30.65	31.01	1.01_2	0.932	99.3
13	109	1.00	171.30	32.62	31.35	0.96_1	0.942	100
14	78	0.72	190.49	13.43	13.81	1.02_8	0.415	44.2
15	55	0.62	198.24	5.68	6.57	1.15_7	0.198	21.1

TABLE III

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL *B* (38.66 GM.)

Run No.	Time to eq. with water vapour, hr.	p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
1	54	1.00	186.62	16.23	14.35	0.88_4	0.371	100
2	68	0.77	190.36	12.49	11.81	0.94_6	0.306	82.5
3	53	0.58	195.10	7.75	7.50	0.96_5	0.194	52.2
5	49	0.47	199.51	3.34	3.48	1.04_2	0.090	25.2
6	72	0.53	196.85	6.00	5.76	0.96_0	0.149	40.2

decrease as the amount adsorbed increases, and finally an abrupt drop in density very close to saturation. While more experimental points would be desirable to define the curves quantitatively, this was not thought necessary to the scope of this paper. In addition the very lengthy period required to accumulate the data had to be considered. However, there appear to be sufficient points to establish the form of the curves with reasonable certainty.

The apparent high density that is observed at low relative pressures is generally attributed to compression of the adsorbate on the active part of the surface (2, p. 420). That the high density results from combination of the water with constituents of the ash is excluded by the determinations on charcoal *D*. Charcoal *D* was prepared from charcoal *C* by leaching out a large portion of the ash, yet reference to Fig. 3 shows that this has not reduced

TABLE IV

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL *C* (34.54 GM.)

Run No.	Time to eq. with water vapour, hr.	p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
1	48	1.00	181.30	23.04	21.62	0.93_9	0.626	100
3	54	0.70	196.30	8.04	8.93	1.11_0	0.259	41.4
4	53	0.72	193.42	10.92	10.85	0.99_4	0.314	50.1
5	49	0.65	198.83	5.51	6.33	1.14_9	0.183	29.2
6	52	0.72	193.44	10.90	10.95	1.00_5	0.317	50.6
7	54	0.74	191.51	12.83	12.80	0.99_8	0.371	59.2
9	54	0.90	182.85	21.49	21.18	0.98_6	0.613	97.9
10	51	0.83*	185.60	18.74	18.37	0.98_1	0.532	85.0

TABLE V

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL *D* (33.33 GM.)

Run No.	Time to eq. with water vapour, hr.	p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
1	51	0.82	188.86	15.89	15.97	1.00_5	0.479	74.5
2	55	0.76	193.63	11.12	12.44	1.11_9	0.373	58.0
4	53	0.76	193.48	11.27	12.20	1.08_2	0.366	56.9
5	54	0.70	197.87	6.88	8.05	1.17_0	0.242	37.5
6	52	0.78	191.99	12.76	13.32	1.04_3	0.400	62.2
8	65	0.94	183.08	21.67	21.15	0.97_6	0.634	98.7
9	52	1.00	181.73	23.02	21.42	0.93_2	0.643	100

TABLE VI

DATA REQUIRED FOR THE APPARENT DENSITY OF WATER ADSORBED ON CHARCOAL *D* (33.33 GM.)—DESORPTION BRANCH OF THE ISOTHERM

Run No.	Desorption time, hr.	Final p/p_0	Final free vol. of cell, cc.	Adsorbed water			x/m	x/x_s, %
				Volume, cc.	Weight, gm.	Apparent density		
1	76	0.53	184.13	20.62	19.52	0.94_6	0.586	91.2
2	75	0.50	191.07	13.68	13.40	0.98_0	0.402	62.5
3	74	0.43	202.09	2.66	2.84	1.06_8	0.085	13.2
4	74	0.47	197.33	7.42	7.32	0.98_7	0.220	34.2
5	74	0.49	190.58	14.17	13.35	0.94_2	0.401	62.4
6	74	0.49	190.50	14.25	13.25	0.93_0	0.398	61.9

Runs 1 to 5—desorption from saturation.
Run 6—desorption from p/p_0 = 0.85.

the apparent density of the water. Also, Danforth and De Vries (6) report high initial densities for carbon tetrachloride and for acetone on charcoal, substances that would not be expected to form complexes analogous to hydrates with the constituents of ash.

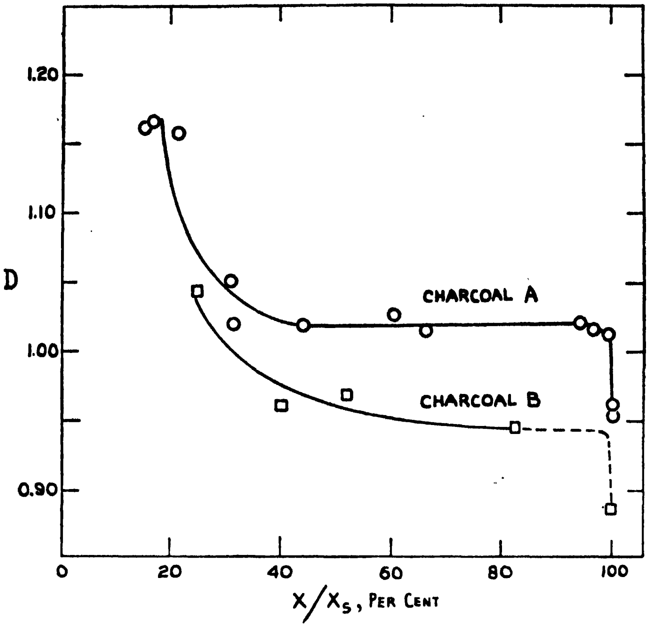

FIG. 2. *Plot of the apparent density of adsorbed water, D, versus the per cent of adsorption at saturation,* x/x_s %, *for charcoals A and B.*

Because the energy change in adsorption, particularly with water adsorbed on charcoal, is relatively small, it is difficult to visualize the adsorbate subjected to large compressional forces. Too, the work of Bangham and coworkers (1) suggests that the adsorbed film is mobile; this would not be expected if it were under high compression. Another explanation, which has not been advanced, is that the apparent high densities arise from the method of measurement. At low relative pressures, it may be presumed that the adsorbate exists as isolated molecules or as small groups of molecules. Under such circumstances, it seems reasonable to expect that the small helium atoms, making up the displaced fluid, may measure more closely the true volume of the water molecules, as distinct from the volume occupied by the water molecules in the liquid state.

There appears to be sufficient experimental evidence to establish the very sudden decrease in the density of the adsorbed water at saturation. With charcoal *B* a mishap, in which the water from the thermostat came in contact with the charcoal, prevented further measurements. However, in view of the results with the other three charcoals, it seems permissible to indicate the drop in density by the dotted portion of the curve in Fig. 2. For an explanation of the sudden decrease in density, it is necessary to make reference to the work of McIntosh *et al.* (10, 11), where it was shown that even when charcoal is immersed in liquid water, a part of the structure is not accessible to the water molecule. This small volume, as determined from the apparent densities of the charcoal in water and in helium, amounts to 0.05 to 0.07 cc. per gm. for the four charcoals studied here. Calculation shows that, if the measured volume of the water at saturation is corrected by such an amount, the sharp drop in the density is practically eliminated*. Perfect agreement would not be expected from such a calculation because there is not a means of determining whether all the very small porous spaces, which are blocked when the charcoal is immersed in liquid water, are blocked when the charcoal is exposed to water vapour at the saturation pressure.

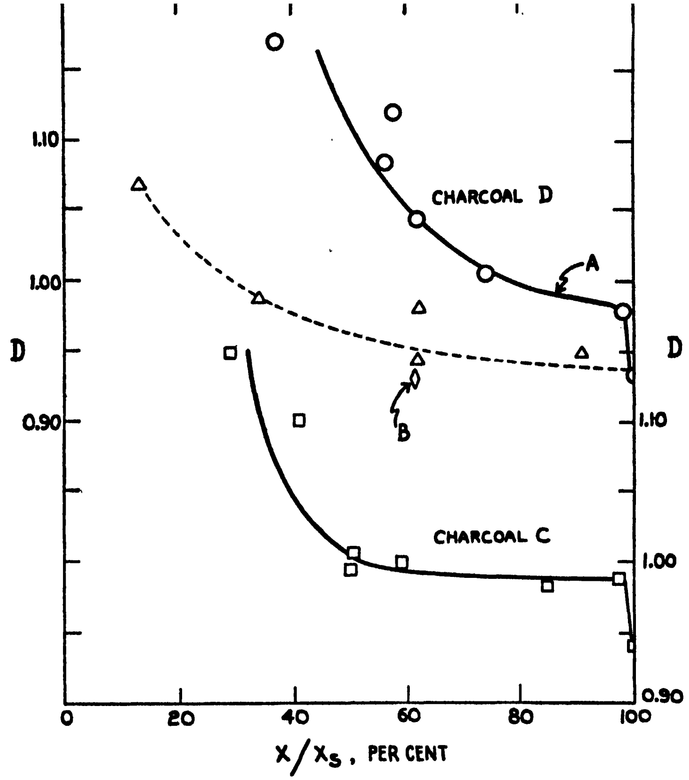

FIG. 3. *Plot of the apparent density of adsorbed water, D, versus the per cent of adsorption at saturation,* x/x_s %, *for charcoals C and D. The dotted curve represents desorption.*

Although the density curves in Figs. 2 and 3 representing adsorption are of similar form, it will be noted that the value of the density just before the drop at saturation is different in each case, ranging from 0.94 for charcoal *B* to 1.02 for charcoal *A*, a somewhat larger variation than might be expected. However, this may be accounted for, if the adsorbed film has a different arrangement on each charcoal. Reference to the data in Table I shows that the volume of porous space, as determined from the densities of the charcoals in helium and in mercury, is larger for charcoal *A* than for charcoal *B*, by a factor of 2.1, while the surface area of charcoal *A* exceeds that of charcoal *B* by a factor of 1.6. This suggests that the average size of the porous spaces is greater for charcoal *A*, and geometric restrictions on the number of adsorbed layers built up would be expected to be less than for charcoal *B*. With charcoals *C* and *D*, where presumably the distribution of sizes of the porous spaces is very similar, the densities of the adsorbed water before the drop at saturation are 0.99 and 0.98, respectively. The nature of the surface may be a factor also, but its effect cannot be determined from these experiments.

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* *In a previous publication (10) it was assumed that the submicro pores became blocked to nitrogen at a relative pressure of 0.87. The validity of that assumption is doubtful in view of the present findings with helium. However, as the measurements in the case of nitrogen were made at −183° C., and with helium at +20° C., it is possible that the blocking of the submicro pores may have occurred at the lower moisture content of the carbon in the experiments with nitrogen.*

The curve of the density of the adsorbed water during desorption, shown in Fig. 3, suggests that there is a distinct difference between the adsorption and desorption mechanisms. The points from which the curve was drawn were obtained by desorbing from saturation. If the sudden drop in density at saturation on the adsorption branch is due to blocking of the very small porous spaces, it appears that the blocking persists during desorption. That the effect is not limited to the desorption from saturation is shown by the last determination in Table VI. The water was adsorbed on the charcoal at a relative pressure of 0.85, and the density of the adsorbed water should have been that indicated by point *A* in Fig. 3. The water was then desorbed to a relative pressure of 0.49, and the determined density is indicated by point *B*, which lies on the desorption curve within experimental error.

It is generally believed that the occurrence of limited hysteresis is an indication of capillary condensation. However, if both the adsorption and desorption processes are governed by a condensation mechanism, the difference in density between the adsorbed water on adsorption and on desorption should not exist. In addition, both branches of the isotherm should have similar slopes. That this is not so is shown by the plot for charcoal *D* in Fig. 4. The only view consistent with experiment seems to be that the adsorption of water takes place on the entire surface of the charcoal, with capillary condensation occurring only very close to the saturation pressure, as indicated by the blocking of the very small porous spaces. Desorption may then occur from menisci in the capillary spaces, the process being governed by the mechanism of condensation.

Brunauer, Deming, Deming, and Teller (3) have sought to include the special case of water adsorption on charcoal within the general multimolecular adsorption theory. To test the applicability of the theory, the adsorption of water on charcoal *A* at low relative pressures was measured. The data are given in Table VII, and the complete isotherm is plotted in Fig. 5. Following the suggestions of Brunauer *et al.* (3), a plot of the data was made in the form $\frac{p}{v\,(p_0-p)}$ versus p/p_0, in order to evaluate the constants V_m

and C of the isotherm equation. The resulting plot was linear only up to a relative pressure of 0.15. From this linear portion, a value of V_m of approximately 100 cc. at S.T.P. and of C of approximately 3.2 was derived. To be consistent with the theory and with the surface area as determined by nitrogen

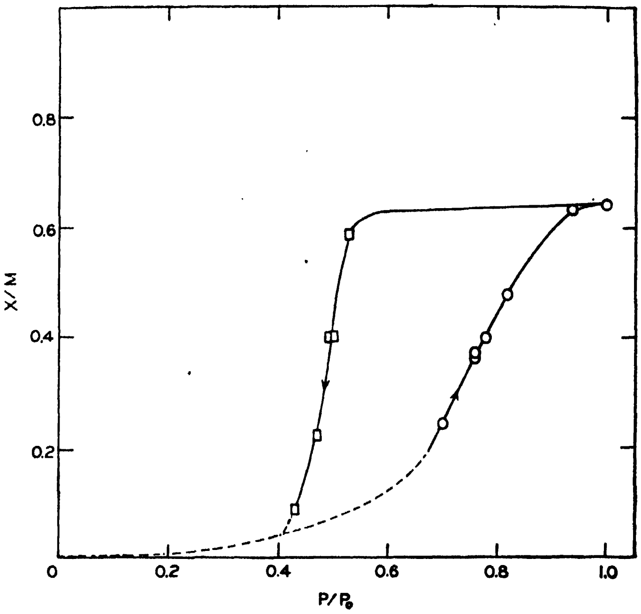

FIG. 4. *The adsorption isotherm of water on charcoal D.*

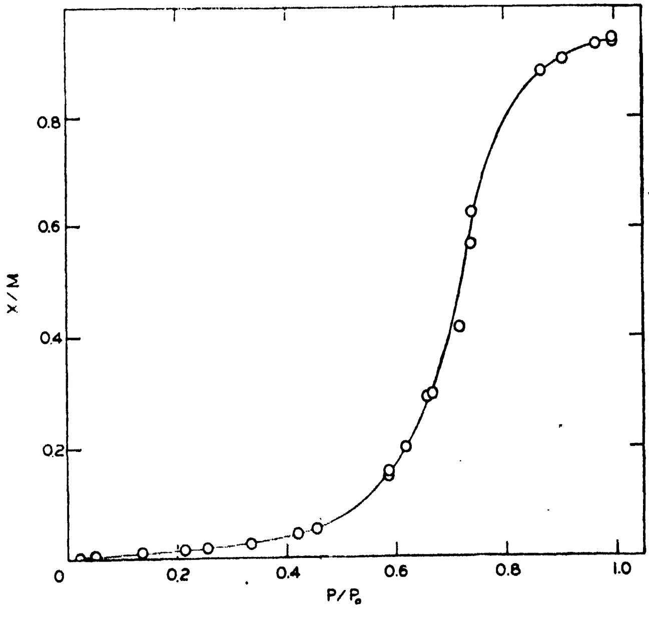

FIG. 5. *The adsorption isotherm of water on charcoal A.*

TABLE VII

ADSORPTION DATA AT LOW RELATIVE HUMIDITIES FOR CHARCOAL *A*

p/p_0	x/m, gm./gm.			
	1	2	3	Average
0.023	0.0039	0.0041	0.0039	0.0040
0.051	0.0062	(0.0071)	0.0063	0.0064
0.137	0.0102	0.0102	0.0100	0.0101
0.257	0.0178	0.0179	0.0175	0.0178
0.337	0.0264	0.0263	0.0261	0.0263
0.422	0.0416	0.0410	0.0410	0.0412
0.217	0.0148	0.0146	0.0150	0.0148
0.456	0.0513	0.0511	0.0511	0.0512

adsorption, V_m should have a value of approximately 700 cc. at S.T.P. and C should be less than unity. Emmett (8) has suggested that, since the *BET* plots are very sensitive to slight variations in C, the reason for the discrepancy may lie in the change in C as the surface is partially covered with water vapour.

Although it is not possible to establish conclusively the mechanism of water adsorption from existing information, it appears worth while to summarize the experimental evidence. The existence of limited hysteresis is the principal point suggesting capillary condensation. The fair agreement between the values of the mean pore radius calculated by either the Cohan formula (5) for adsorption or the Kelvin equation for desorption with that determined from the ratio of the total internal volume to the total surface area supports this view. However, the expansion of the charcoal when water vapour is adsorbed (14) suggests that the mechanism of adsorption does not differ markedly from that by which other vapours are adsorbed. The marked difference in density of the adsorbed phase established during adsorption from that established during desorption is most easily explained by assuming the formation of menisci at saturation or on desorption. Also, the high values of the density of the water adsorbed at low relative pressures suggest that the formation of a non-continuous film is the first step in the adsorption process.

Acknowledgment

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THE INFLUENCE OF MEMBRANE PREPARATION ON THE OSMOTIC PRESSURE OF POLYVINYL ACETATE IN ACETONE[1]

By R. E. Robertson[2], R. McIntosh[3], and W. E. Grummitt[4]

Abstract

A full account of the experimental procedures used to determine the number average molecular weights of a series of polyvinyl acetates is given. Adsorption of polyvinyl acetate on a cellophane membrane is demonstrated. The importance of this phenomenon is increased when cells of large ratio of membrane surface to cell volume are used. The presence of small amounts of sodium hydroxide in the membrane eliminates detectable adsorption and alters the osmotic pressure values. This change does not appear to be due to imperfect semipermeability of the membranes, and no adequate explanation of the phenomenon has been as yet discovered.

In the past several years the publications of Flory and Huggins, Mark and others* have developed considerably the theoretical aspects of the behaviour of macromolecules in solution. At the same time improvements in the design of osmotic cells have decreased the difficulty of such determinations (9, 10, 19) until the evaluation of the number average molecular weight of macromolecules appears straightforward. However, a good deal remains unknown concerning the mechanism by which the semipermeable membrane functions (see, for example, Fuoss and Mead (10)) and the choice and preparation of such membranes still appears arbitrary. Some authors, notably Carter and Record (7), have found cellophane membranes satisfactory, while others have remarked that such membranes were found unsuitable (19) but have not stated wherein the difficulty lay. At the same time such factors as the time lags involved in the establishment of equilibrium pressures have not been adequately explained.

In an attempt to demonstrate that changes of viscosity of solutions of polymers could be attributed to molecular weight changes (see another paper in this series), an osmometer was constructed similar to others that have already been described. It became evident immediately that factors of importance from the experimental viewpoint had not been adequately assessed in other publications, or were not operative under slightly different experimental conditions. These factors made necessary an extensive investigation into the preparation of cellophane membranes and the influence of that preparation on the results obtained. Since a complete explanation of certain results has not been possible, a very full description of the experimental methods and findings is given below.

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The results were obtained on polyvinyl acetate dissolved in acetone, but certain evidence exists that similar phenomena may be found with other polymer–solvent systems. To sum up the conclusions reached in studying the polyvinyl-acetate–acetone system, it appears that:

1. Adsorption of polymer occurs on the cellophane membranes when the membranes are prepared by the Carter and Record method.

2. The amount of adsorption is sufficient in cells of large ratio of membrane surface to cell volume to cause large errors in the molecular weight values that are obtained.

3. Time lags in the establishment of equilibrium osmotic pressures are caused mainly by the adsorption process.

4. Adsorption may be decreased to inappreciable amounts by treating the cellophane membranes in caustic solution before accommodation to the organic solvent, provided that treatment subsequent to the caustic wash does not remove all the alkali from the membrane. The amount that must be retained on the membrane is not known exactly, but relatively wide variation of the washing treatment does not appear to alter the membrane behaviour appreciably.

5. Molecular weight values may be obtained with membranes prepared by the Carter and Record method by permitting adsorption to occur and then refilling the cell several times with fresh solution of the same concentration.

6. The molecular weights obtained as described in 5 do not correspond with those obtained using caustic treated membranes, and the results cannot be explained by a difference in permeability of the membranes to small molecular weight material.

Since these points require careful substantiation, and since it is necessary to show that the results do not depend upon the heterogeneity of the polymer samples in an obvious manner, a full account of the experimental equipment and procedures follows.

Experimental

Polymers

Commercial samples of polyvinyl acetate were used throughout the investigation. No attempt was made to prepare homogeneous materials. Insoluble polymer was removed from the samples by dissolving them in acetone and filtering carefully. After filtration the polymer was precipitated from the acetone solution (5% by weight) by pouring it slowly into water. The water was stirred and the polymer collected around the stirrer, from which it was removed periodically. The precipitated polymer was partially dried by prolonged evacuation at room temperature. When in this partially dried state it was cut into small pieces and then dried thoroughly by vigorous evacuation and stored over Drierite. One large sample of each grade of polymer was prepared in this way and the same preparation was used throughout the investigation.

Acetone

Both reagent grade and c.p. acetone, which was stored over Drierite, were used. No variation in behaviour between different batches of acetone was ever observed.

Osmometer

A dynamic type of osmometer similar in design to that of Van Campen (6) and Montonna and Jilk (19) was used (Fig. 1). The operation of such an osmometer using a counter pressure manometer has been fully described by Carter and Record (7). In dealing with heterogeneous samples, this type of osmometer offers certain advantages. Chief of these is the use of relatively high concentrations of polymer; this enables one to ensure that the membrane is semipermeable. A second advantage is that the relative permeability of the membrane to solvent is given directly by the slope of the line representing rate of movement of the meniscus as a function of pressure. This measurement was essential in establishing the characteristics of the membrane before and during its use with solutions.

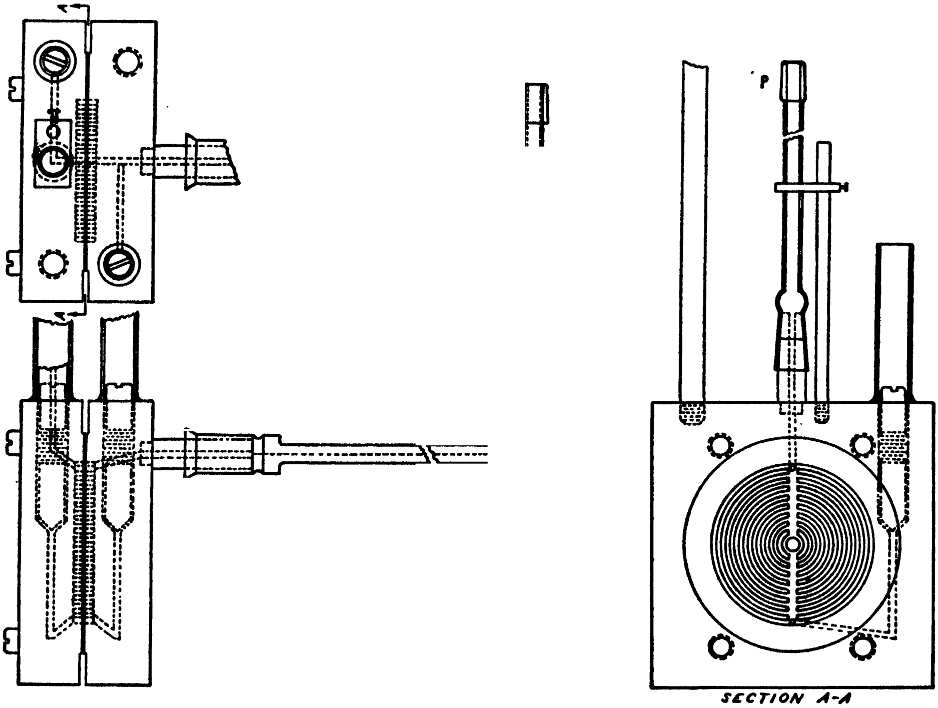

FIG. 1. *Dynamic osmotic cell.*

The disadvantages of this type of cell were the tediousness of making measurements, the very precise temperature control required (temperature fluctuations of 0.001° C. are easily detected by variations in the rate of meniscus movement) and the relatively long extrapolation of the π/C versus C plots to zero concentration.

In common with the cell recently described by Fuoss and Mead (10) and that used by Flory (9), the ratio of membrane area to cell volume is large. It is this fact that led to the discovery of the adsorption effects, and a large value of the ratio of area to volume is therefore a serious disadvantage of these cells if adsorption occurs on other types of membranes and with other polymer–solvent systems. A table of estimated values of the area–volume ratio for several cells is given in Table I.

TABLE I

AREA–VOLUME RATIO OF OSMOMETERS

Osmometer	Membrane surface/ cell volume, cm.$^{-1}$
Van Campen cell (6)	20.
Meyer, Wolff and Boissonnas (18)	2.0
Fuoss and Mead (10)	5.0
Carter and Record (7)	1.6
Flory (9)	3.1
Cell used in this investigation	4.5

Thermostat Control System

The required temperature control was obtained with the following arrangement. A large metal bath containing 10 gal. of transformer oil was completely enclosed in an air-bath maintained at about 29° C. In the oil-bath proper was placed a Wheatstone bridge, two arms of which were manganin and two iron. A galvanometer (0.0049 μamp. per mm.) was connected across the bridge, the other ends of which were connected with a 6 v. storage battery. The resistances of the arms (about 450 Ω) were adjusted roughly to bring the bridge to balance at 30° C. Final adjustment of resistance was made on a thermostatically controlled Leeds and Northrup resistance box in series with one of the manganin arms. An electric heater of about 3 w. capacity was employed in the oil-bath, and was controlled by a photoelectric relay actuated by the light spot from the galvanometer. The heating period of the bath was interrupted by a shutter operating in front of the photoelectric cells, as suggested by Eichelburger (8). Calculation of the thermostat temperature variations from a knowledge of the heating period, the heater input, and the thermal capacity of the bath showed a control of 8/10,000° C. This calculation was found to check with experiment, which showed a maximum deviation of 7/10,000° C. The performance of the thermostat was extremely reliable; this was partly due to very good stirring.

Membranes

Two types of membrane were employed, designated hereafter as Carter and Record membranes and as caustic treated membranes, respectively.

Both these types were prepared from No. 600 P.T. Cellophane (not waterproofed) supplied by Canadian Industries Ltd.

To prepare the *C* and *R** membranes the cellophane was first washed several times with warm water to remove plasticizers. The permeability of the membrane to solvent was then established by soaking in ethyl-alcohol–water solutions. Low permeabilities were obtained by soaking in solutions of high alcohol content, and high permeabilities by soaking in solutions of high water content exactly as described by Carter and Record. Before transfer to anhydrous acetone the membranes were stored in anhydrous ethanol for a given period. Too long storage in anhydrous ethanol reduced the permeability, and a fixed period for this stage of the preparation (12 hr.) was used. No change in permeability with time occurred on storage in anhydrous acetone.

The preparation of caustic treated membranes was somewhat similar. The membrane was first soaked in warm water and then in a solution of known concentration of caustic for a given time at room temperature. The permeability to solvent was established at this step as shown in Table II. The influence of the time of soaking in the caustic solution on the permeability was not examined thoroughly, but appears to be of lesser importance than the concentration. Excess caustic was then removed by dipping either in water or 50 : 50 ethanol–water. The membranes were then stored for 15 min. in anhydrous ethanol, and finally transferred to anhydrous acetone.

TABLE II

PERMEABILITY OF CAUSTIC TREATED CELLOPHANE TO ACETONE AT 30° C.**

NaOH, %	Time at 25° C., min.	d, cm. × 10^3†	$P \times 10^{13}$‡
2	15	7.5	9.0
4	15	9.0	12.0
6	15	(14.6)	16.4
8	15	14.0	21.0
10	30	10.0	36.0

** *Canadian Industries Ltd. Cellophane No. 600 P.T.*

† *Thickness of membrane.*

‡ P = *specific permeability defined by Manegold and co-workers (3, 16) by the equation* $P = D\eta d$.

D = *cc./cm.²/sec. for a pressure of 1 dyne/cm.²*

η = *viscosity of the solvent in poises.*

The presence of caustic in the membranes was established by burning off the cellophane and testing the water extract of the ash. Whenever all the caustic had been removed from the membrane, its behaviour was similar to that of a *C* and *R* membrane, except that its permeability to solvent was greater and it was no longer semipermeable to low molecular weight polymer.

**Carter and Record, Ref. (7).*

So long as caustic was left in the membrane, its behaviour was different from that of a C and R membrane. The semipermeability of the membrane persisted at values of solvent permeability nearly 50 times greater than a semipermeable C and R membrane. Thus, with a C and R membrane the small molecular weight material could be detected in the solvent half-cell when a sample of Gelva 15 was used if the specific permeability exceeded a value of 0.35×10^{-13}. With a caustic treated membrane no polymer from a similar solution could be detected when the permeability was 16.4×10^{-13}. Obviously, in using higher molecular weight grades, semipermeability was more easily obtained with both types of membrane. For Gelva 360, a fully swollen C and R membrane could be used, but, for Gelva 45, membranes of lower solvent permeability were required. Properly prepared, caustic membranes (up to 6% sodium hydroxide for 15 min.) were found to be semipermeable to all types of polymer grade studied. Two tests for semipermeability were employed. In the first, the contents of the solvent half-cell was pipetted into an aluminium weighing bottle of known weight, and the thimble and contents quickly weighed. The sample was then evaporated to dryness and the container again weighed. Blank determinations permitted correction for any corrosion of the brass osmometer cell.

The second test was found to be somewhat more sensitive and more convenient. In this case the contents of the solvent half-cell was run into a small beaker of water. The appearance of turbidity indicated that polymer was present. Quantitative tests with this procedure showed that a solution of 0.01% concentration by weight could be detected with certainty and of 0.005% concentration by weight gave a very faint cloud. Since in testing any membrane for semipermeability a solution of 3% by weight was placed in the solution half-cell, a membrane designated as semipermeable allows less than 0.2% of the concentration in the solution side to diffuse through the membrane.

Equilibrium Osmotic Pressures

The time to constant osmotic pressure was established for both C and R and caustic treated membranes. The time to final pressure was between six and eight hours for the C and R membranes, in agreement with that reported by other investigators, and about one-half hour, or almost exactly the time for thermal equilibrium to be established, for the caustic treated membranes. No downward drift with time was ever observed with either type of membrane, although values were taken for as long as 72 hr. in some cases. From the criteria of semipermeability of the membranes and the constancy of osmotic pressure with time, values obtained with either type of membrane should be true osmotic values.

Intrinsic Viscosities

Intrinsic viscosities were measured in the ordinary manner by means of an Ostwald type viscometer. A kinetic energy correction was applied, and amounted to about 6% in the worst case.

Preparation and Handling of Solutions

All solutions were made up by weight and recalculated in terms of grams per 100 cc. of solution, from a knowledge of the density of pure acetone at the temperature of the measurement. Both in the case of viscosity and osmotic determinations the densities of the solutions were assumed to be the same as that of pure acetone.

In filling the viscometer and the osmometer at least four rinses were always employed, and this number was found to be sufficient. In handling the solutions, transfer was made by blowing the liquid into the receptacle by dried filtered air.

Results

Adsorption Effects on Carter and Record Type Membranes

Osmotic pressure measurements made with *C* and *R* membranes gave fair rectilinear plots of π/C versus C for Gelvas 360, 150, 45, and 15. Contrary, however, to the predictions of relative molecular weights from intrinsic viscosity measurements (see Table VIII), grades 150, 45, and 15 gave π/C values that were equal to or lower than corresponding values for 360. The results given in Table III were all equilibrium values and no polymer was

TABLE III

OSMOTIC DETERMINATIONS WITH CARTER-RECORD MEMBRANES

Conc., gm./100cc.	μ*	π, gm./cm.^{2}	π/C	Remarks	Conc., gm./100cc.	μ*	π, gm./cm.^{2}	π/C	Remarks
Gelva 360					Gelva 150				
2.88	0.46	15.40	5.35		1.31	0.58	4.52	3.45	
1.95	0.46	9.12	4.67		2.84$_5$	0.50	19.60	6.90	
5.61	0.21	70.60	12.60		4.24	0.22	41.80	9.88	
3.86	0.29	34.00	8.60	$(\pi/C)_{c=0} = 0.62$	1.40	0.23	5.02	3.58	$(\pi/C)_{c=0} = 0.65$
3.95	0.26	36.40	9.22		3.17	0.25	16.48	5.20	
2.57	0.57	15.25	5.94		3.31	0.25	25.45	7.70	
1.28	0.62	4.40	3.44		1.76	0.23	7.97	4.50	
3.47	0.44	27.60	7.96		1.91$_5$	0.50	8.60	4.49	
Gelva 45					Gelva 15				
1.69	0.22	6.52	3.65		1.60	0.22	5.55	3.47	Low
3.05	0.21	21.21	7.07	$(\pi/C)_{c=0} = 0.285$	2.38	0.18	18.20	7.65	
							17.70	7.44	
4.12	0.20	37.20	9.05		1.97	0.18	13.35	6.77	
					1.25	0.19	4.58	3.65	$(\pi/C)_{c=0} = 0.40$
					0.79	—	2.19	2.77	
					3.11	0.16	35.20	11.30	
					1.59	0.24	10.72	6.74	

* *These values represent the permeability of the membrane to solvent determined with solution in one half-cell, and are not corrected for membrane thickness, and have obviously not been converted into the units of specific permeability.*

detected in the solvent half-cell. The results were also reproducible provided that the same experimental procedures were followed. In all instances there was a long time lag of between six and eight hours while the osmotic pressure built up to its equilibrium value. Similar time lags had been noted by Flory (9), Gee (11), Gee and Treloar (12), and Carter and Record (7).

An attempt to determine the cause of these anomalous results was made by washing out the solution half-cell with more solution of the same concentration after the first equilibrium value had been attained. This treatment brought to light two phenomena. First, the time to equilibrium pressure was sharply reduced, in the case of low permeability membranes, to a period of approximately one-half hour. For high permeability membranes the reduction was not as marked and although not determined precisely time lags of about two to three hours duration were still observed. Second, the equilibrium osmotic pressure was increased over that recorded in Table III, as shown in Table IV. This was not true of the values for grade 360, probably owing to

TABLE IV

DATA ILLUSTRATING THE "WASHING-UP" EFFECT WITH CARTER-RECORD MEMBRANES

Gelva	Conc., gm./100 cc.	Filling	π, gm./cm.^{2}	π/C	Membrane
45	0.934	1	—	(2.26)	Carter–Record
		2 3	3.74	4.01	Low permeability
	1.38_6	1		(3.24)	No polymer was detected diffusing to solvent side
		2 3	6.74	4.85	
	1.67	1	—	(4.85)	
		2 3	9.23	5.48	
	2.54	1	—	(5.66)	
		2 3	18.20	7.16	
	0.0	—	—	(2.14)	
150	2.98	3	22.20	7.45	Membrane *C* and *R* fully swollen.
	2.45	3	14.70	6.00	Not completely semipermeable to this grade.
	2.01	3	10.40	5.18	
	1.64	2	7.46	4.55	
	0.0	—	—	(1.08)	
360	1.19	1	—		
		2 3	3.36	2.82	Same as for 45 above.
	1.65	1		(3.31)	
		2 3	6.12	3.70	
	2.41	1		(4.62)	
		2 3	12.12	5.04	
	0.0			(0.62)	

the fact that in determining them the solution side was not washed free of polymer before being filled with a new solution, and probably also because the effect is of lesser importance with the higher polymer grades. These observations served to explain the reproducibility of the results in Table III for identical experimental procedures, and to indicate that the reason for anomalous results and extended time lags was adsorption at the membrane surface. Finally, if the procedure of allowing adsorption to occur and then washing the cell again were followed, differentiation of the polymer grades in conformity with intrinsic viscosity values was possible.

Results Obtained with Caustic Treated Membranes

Before the reason for the behaviour of *C* and *R* membranes had been determined, membranes prepared by caustic treatment were used. With these membranes the time lags to equilibrium pressure were negligible since constant readings were obtained as soon as thermal equilibrium had been established (one-half hour). This suggests that adsorption at the membrane does not occur. This is supported by two considerations, namely, that differentiation of the polymer grades in the order suggested by viscosity is possible without repeated washings, and, second, that washing of the solution half-cell does not increase the equilibrium value of the osmotic pressure. This last is illustrated in Table VII, where values for grades 15, 150, and 1700 with two caustic membranes of different preparation are given.

Data on five polymer grades obtained with caustic treated membranes are given in Table V. These data are plotted in Fig. 2.

TABLE V

OSMOTIC PRESSURE MEASUREMENTS ON A SERIES OF GELVAS WITH CAUSTIC TREATED MEMBRANES

Conc., gm./100 cc.	Conc. in solvent half-cell	Membrane	Permeability to solvent	π, gm./cm.^{2}	π/C	M_n
Gelva 1700						
0.75_5	0	2% caustic 50/50 alcohol-water wash	0.3*	1.26	1.67	
1.17	0		0.3*	2.22	1.90	
1.42_5	0		0.3*	2.46		
1.56	0	1.5% caustic water wash	0.43*	4.52	2.90	8.5×10^5
0.91	0	3% caustic water wash	0.70*	1.61	1.77	
0.00	—	—	—	—	(0.30)	

* *The starred values represent the permeability of the membrane to solvent, uncorrected for membrane thickness, with solvent in both half-cells; the unstarred values represent the measurements made with solution in one-half cell.*

TABLE V

OSMOTIC PRESSURE MEASUREMENTS ON A SERIES OF GELVAS WITH CAUSTIC TREATED MEMBRANES —*Concluded*

Conc., gm./100 cc.	Conc. in solvent half-cell	Membrane	Permeability to solvent	π, gm./cm.^{2}	π/C	M_n
Gelva 360						
1.08$_5$	0	4% caustic water wash	0.92	2.61	2.40	
2.27	0		0.82	9.27	4.08	
1.03	0	10% caustic water wash	2.54	2.21	2.14	
1.86	0		2.42	6.54	3.51	
1.42	0		—	4.10	2.91	4.1 × 10^5
0.00	—		—	—	(0.62)	
Gelva 150						
0.788	0	8% caustic water wash	1.24	1.92	2.44	
1.11	0		1.18	3.48	3.14	
1.70	0		—	6.80	4.00	
1.56	0	1.5% caustic water wash	0.53*	5.91	3.79	
2.01	0		—	8.65	4.31	
2.50	0		—	13.4	5.36	
(0.00)	—	—	—	—	(1.28)	2.0 × 10^5
Gelva 45						
0.97$_5$	0	10% caustic water wash	2.68	3.18	3.26	
1.45	0		2.46	5.74	3.95	
1.68	0		2.30	7.76	4.61	
1.98	0		2.32	9.81	4.95	
2.22	0		2.10	11.88	5.35	
(0.00)	—	—	—	—	(1.74)	1.47 × 10^5
Gelva 15						
2.06	0	4% caustic water wash	—	15.20	7.39	
2.06	0		9.7	15.25		
0.60	0		0.9	3.13	5.20	
2.78	0		0.8	23.2	8.35	
1.69	0	6% caustic water wash	1.0	11.39	6.71	
2.32	0		0.97	17.68	7.61	
1.25	0		0.96	7.45	5.96	
0.824	0		1.0	4.67	5.69	
0.0	—	—	—	—	(4.20)	6.1 × 10^4
1.00	Slightly permeable	8% caustic water wash	1.4	4.95	4.95	
1.68			1.2	9.95	5.92	
2.37			1.06	22.60	9.55	
0.0	—	—	—	—	(4.01)	6.4 × 10^4
2.28	Definitely permeable	10% caustic water wash	2.8	15.30	6.71	
1.77			2.6	9.66	5.46	
0.957			2.8	3.61	3.77	
2.36			2.5	15.65	6.64	9.3 × 10^4
2.36				16.60	7.04	
0.0	—	—	—	—	(2.76)	

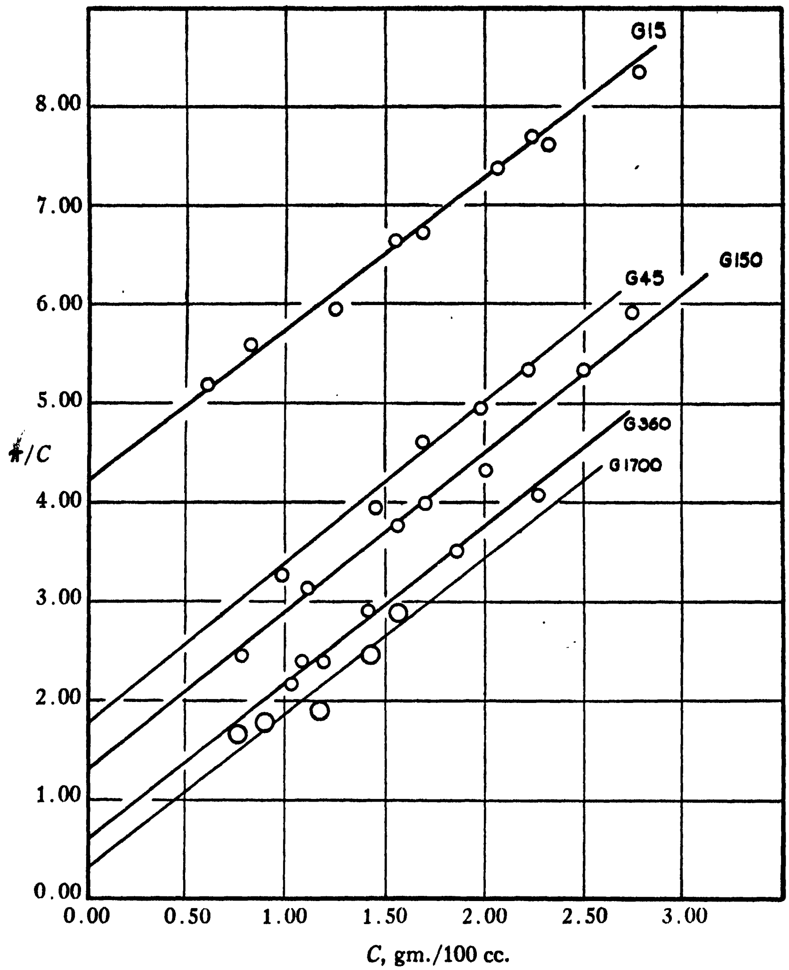

FIG. 2. *Osmotic pressure concentration ratio vs. concentration for a series of Gelvas.*

Comparison of Values Obtained with C and R Membranes and Caustic Treated Membranes

Typical data illustrating the difference in behaviour of the two types of membrane are given in Table VI. In Fig. 3 the values obtained for grades 45, 150, and 360 with *C* and *R* membranes by continued rinsing of the solution half-cell are compared with those obtained using caustic treated membranes.

Viscometric Results

In Table VIII are recorded data from which the intrinsic viscosity of the various polymer grades was calculated. The values of k', the constant characteristic of the solute–solvent system as suggested by Huggins (15), are given in Table IX along with the intrinsic viscosity and the number average molecular weights obtained with caustic treated membranes. It is to be

TABLE VI

SUMMARY OF OSMOTIC DATA FOR A SERIES OF GELVAS ILLUSTRATING THE EFFECT OF ADSORPTION

Gelva	Membrane	Number of** determinations	Time to reach equilibrium, hr.	$(\pi/C)_{c=0}$	Slope of π/C vs. C
360	Carter–Record	1	6 – 8	0.62	2.12
	Carter–Record	3	About ½*	0.72	
	Caustic	1	About 1 – 2	0.62	1.57
150	Carter–Record	1	6 – 8	0.65	2.12
	Carter–Record	3	About ½*	1.08	2.08
	Caustic	1	About ½	1.28	1.55
45	Carter–Record	1	6 – 8	0.28	2.08
	Carter–Record	3	About ½*	2.14	1.99
	Caustic	1	About ½	1.84	1.58
15	Carter–Record	1	6 – 8	0.45	3.16
	Caustic	1	About ½	4.20	1.54
	Caustic	3	About ½	4.20	1.54

* *These data are for low permeability Carter–Record membranes. Somewhat longer times to reach equilibrium (~ one to two hours) were found with more permeable membranes of this type, even after repeated washings.*

** *The numbers refer to the number of equilibrium values successively determined with each concentration.*

TABLE VII

EFFECT OF REPEATED DETERMINATIONS WITH CAUSTIC MEMBRANES

Gelva	Conc., gm./100cc.	Conc. on solvent side	Membrane	*μ to solvent	π, gm./cm.²	π/C	Filling
15	1.55	0	2% caustic washed	0.30	10.2_0	6.64	1st
		0	with 50 : 50 alcohol	0.30	10.34	6.69	3rd
	2.23	0		0.30	17.15	7.69	1st
				0.30	17.1	7.68	3rd
150	1.56	0	1.5% caustic washed	0.53	8.65	4.31	1st
		0	with water	0.53	8.70	4.34	2nd
1700	1.56	0	1.5% caustic washed	0.53	4.52	2.90	1st
			with water	0.53	4.50	2.89	2nd

* *Permeability to solvent, not corrected for membrane thickness, with solvent in both half-cells.*

noted that k' does not vary appreciably throughout the series, even for a "reacetylated" sample, which is known to differ in certain respects from material which has not been hydrolysed and then reconverted to the acetate (4). Since k' depends both upon solute and solvent, it cannot be stated that a like constancy of k' would be observed in other solvents.

Relation Between Intrinsic Viscosity and Number Average Molecular Weight

The modified form of the Staudinger equation $[\eta] = KM^a$ was probably first suggested by Mark (17, p. 103) and has been repeatedly verified by Houwink (14) from data of Staudinger and Warth (20) on heterogeneous samples, by Flory (9) and Mark and co-workers (1, 2) for fractionated polymers. On the assumption that each grade of this series of samples has the same degree of heterogeneity, a straight line is to be anticipated for a plot of log $[\eta]$ versus log M_n (Fig. 4). The slope of this line determines a in the above equation, and gives a value of 0.63, in excellent agreement with values obtained by Houwink, Flory, etc. The value of K will depend upon the degree of heterogeneity of the samples and therefore cannot be compared with other published values.

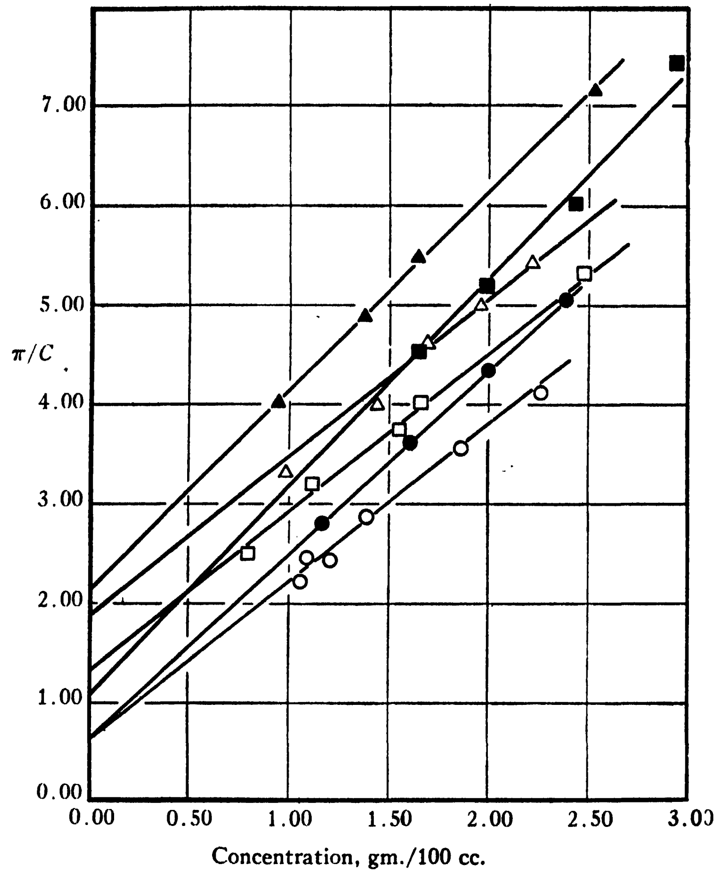

FIG. 3. *Variation in osmotic-pressure–concentration ratio with concentration for two kinds of membrane.*

	G 45	*G 150*	*G 360*
Carter–Record membrane	▲	■	●
Caustic membrane	△	□	○

TABLE VIII

SUMMARY OF VISCOSITY DATA FOR A SERIES OF GELVAS

Gelva	Conc., gm./100 cc.	$\frac{\log \eta}{C}$	Gelva	Conc., gm./100 cc.	$\frac{\log \eta}{C}$
1700	0.1475	3.14	145	0.181	1.33
	0.2085	3.08		0.437	1.25
	0.2955	2.86		0.716	1.185
	0.503	2.78		0.779	1.12
	0.600	2.60		(0.0)	(1.390)
	(0.0)	(3.325)			
360	0.160	2.100	45 Reacetylated	0.165	1.054
	0.432	1.933		0.422	1.024
	0.704	1.760		0.708	0.915
	0.872	1.600		0.980	0.894
	0.0	(2.240)		(0.0)	(1.085)
150	0.133	1.74	45	0.284	0.980
	0.167	1.77		0.357	0.964
	0.290	1.71		0.414	0.965
	0.393	1.62		0.651	0.926
	0.526	1.57		0.955	0.884
	0.654	1.50		(0.0)	(1.06)
	0.0	(1.87)			
			15	0.195	0.636
				0.351	0.613
				0.492	0.640
				0.656	0.610
				0.0	0.605
					(0.650)

TABLE IX

VALUES OF INTRINSIC VISCOSITY, k', AND M_n, FOR A SERIES OF GELVAS

Gelva	$[\eta]$	k'	M_n
15	0.65	0.31	6.10×10^4
45	1.06	0.31	1.47×10^5
45 Reacetylated	1.085	0.33	—
145	1.39	0.33	—
150	1.87	0.34	2.00×10^5
360	2.24	0.35	4.12×10^5
1700	3.32_5	0.35	8.5×10^5

In passing, it is interesting to note that the commercial samples reported on here should have approximately the same degree of heterogeneity over the wide range of average molecular weight studied.

Discussion

The existence of adsorption phenomena on cellophane membranes has been determined only for polyvinyl acetate in acetone. Some evidence exists, however, that this effect may be present in other systems. Fuoss and Mead

(10) adopted a technique of accommodating cell and membrane to polymer solution in order to avoid adsorption effects in dealing with polyvinyl chloride in methyl amyl ketone. Moreover, these authors have remarked that in their view a membrane is not suitable unless it is swollen by the solvent employed, and have suggested that the reason lies in the necessity of the establishment of a phase consisting of solvent and membrane between the two half-cells. An alternative explanation is possible in view of adsorption of solute at the membrane. If the membrane is such that it may be readily swollen by solvent, the unsaturated forces in its surface will be preferentially satisfied by solvent, and no adsorption of solute will occur.

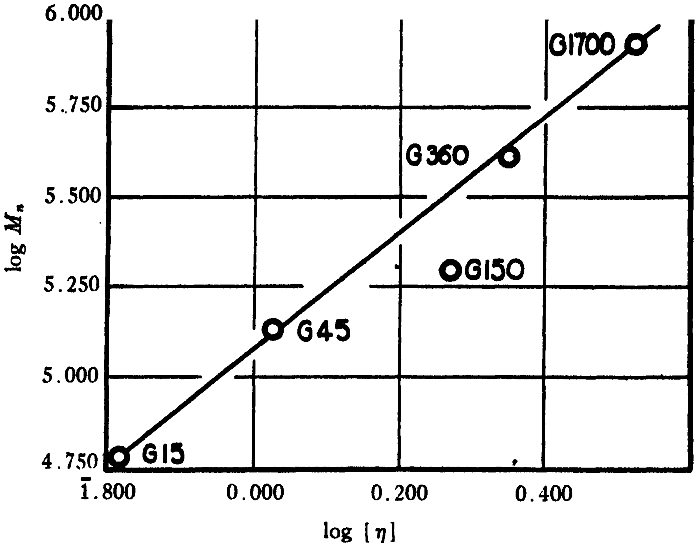

FIG. 4. *Log M_n vs log [η] for a series of Gelvas.*

The most suggestive evidence that adsorption may occur with other polymer–solvent–membrane systems is the frequent reporting of extended time lags (see above). These time lags have been reduced by stirring mechanisms (7), but never completely eliminated, a fact that has not been readily explained. From the present investigation it is suggested that these time lags may be due to the adsorptive process at the membrane interface.

The second point of interest is the difference in osmotic pressure values determined with Carter and Record membranes and with caustic treated membranes. As the preparation of a truly semipermeable membrane was always easier with a caustic treated type, and as both types of membrane are semipermeable within the sensitivity of the tests already described, the difference in values does not appear to be due to this factor. Since the values with *C* and *R* membranes are always higher, this type of membrane would be expected to be more nearly perfectly semipermeable than caustic treated ones, while just the reverse was found in practice. A striking example of this is seen in Fig. 3, where the values for Gelva 150 were obtained with a *C* and *R* type membrane which gave a very faint cloud when tested for semipermeability. As anticipated, therefore, the intercept in the figure lies below that determined with a semipermeable caustic treated membrane. At ordinary concentrations, however, the values for this membrane lie above those obtained with the caustic treated membrane.

Because of the rapidity with which equilibrium is established using caustic treated membranes, we have supposed these values to represent the true osmotic pressures. On this assumption, and, remembering that the relation between osmotic pressure and concentration is of the form $\pi = Ac + Bc^2$ in the concentration range studied, it appears empirically that an effective concentration greater than the nominal concentration is established in the case of *C* and *R* treated membranes where repeated rinsings have been made. On this basis both the difference in intercept and in slope of the π/c versus c plots is accounted for. However, reference to the values obtained when the membrane is not truly semipermeable shows that the slope of the π/c versus c plot is still greater than a caustic treated membrane, although the actual concentration must be less than the nominal.

No explanation for this behaviour in terms of the known properties of solutions and rules of adsorption at interfaces is possible. The assumption of positive adsorption of solvent at the membrane would explain the results, but as positive adsorption of solute has been indicated by experiment, this hypothesis is not tenable. More precise measurements at lower concentrations are obviously required, and, until these have been made, it appears best to consider that a true equilibrium measurement has not been made in one or the other series of experiments.

One further observation requires emphasis. As indicated in certain of the tables, the permeability of both types of membranes to solvent varies in a regular manner with the concentration of the solution being studied. This was first thought to be caused by the adsorption on the membrane, but does not appear likely since both types of membrane exhibit roughly the same behaviour. Increased viscosity of the material passing through the membrane due to the presence of small amounts of low molecular weight polymer is also a possibility, but, in view of the negative turbidity tests, this requires substantiation by further experiment.

Acknowledgment

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THE FLOW OF GASES AND VAPOURS THROUGH POROUS MEDIA[1]

By J. W. Hodgins[2], E. A. Flood[3], and J. R. Dacey[4]

Abstract

A study has been made of the flow of permanent gases (helium, hydrogen, nitrogen) and condensable vapours (diethyl ether and ethyl bromide) through a sintered glass plug. The permanent gases are transferred by a combination of Knudsen and Poiseuille flow, while the flow of condensable vapours diverges from these equations in such a fashion as to suggest surface transfer.

The flow rates of the condensable vapours begin to fall off at about 50% of the saturation pressures. Hysteresis effects are also observed in this region. It is suggested that these phenomena are caused by the condensation of small amounts of vapour in critical regions of the glass structure.

Introduction

High-boiling compounds are, in general, much more strongly adsorbed than are permanent gases, which have low boiling points. As a consequence, the adsorbed layer of a high-boiling vapour is much thicker on the adsorbent at a given temperature and pressure, and in extremely fine capillaries liquid can exist below the saturation pressure.

If a high-boiling gas or condensable vapour be forced by a pressure gradient through a medium consisting of a multitude of minute pores, it is a reasonable supposition that the adsorbed layer of vapour may cause the mobility through the pores to be different than if no adsorption occurred.

At the outset, an investigation was initiated to compare the rates of transfer of high-boiling vapours with those of permanent gases, when the vapours were forced to flow through rods of activated charcoal. The transfer rate of condensable vapours through the charcoal was found to be higher relative to the rate for permanent gases than had been expected, and divergence from Knudsen flow at low pressures was observed. However, after a series of preliminary experiments, it became apparent that knowledge of the flow characteristics through a low activity medium was desirable. Therefore, the diffusion of vapours and permanent gases through plugs of sintered glass was investigated, and this paper is a description of those experiments.

Experimental

(A) Apparatus

1. *Sintered Glass Plugs*

Pyrex glass (S.G. 2.23) was ground in an agate mortar to −100 Tyler mesh, and then ball-milled with flint stones for 12 hr. After treatment with

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hot nitric acid and thorough washing with water, the material was dried. The size spectrum of the Pyrex particles, determined microscopically, was as follows:

Particle diameter, microns	60–51	50–41	40–31	30–21	20–11	10–1.7
Number of particles in class	1	4	4	14	21	54

The average particle diameter was 12.3 μ. These particles were irregularly shaped, and for this reason each measurement was taken in the same direction, on the theory that if a sufficient number of particles were counted, the average particle diameter obtained would be correct. Most of the particles were roughly spherical—that is, no one dimension was greatly in excess of any other.

The glass powder was poured into a circular graphite mould and sintered at 650°C. into a rod 22.1 mm. long and 8.6 mm. in diameter. The plug was then sealed into a glass tube having a female 14/35 standard taper on one end. The heat required to seal the plug into the glass tube fused the periphery of the sintered glass, and thus reduced the diameter of the porous glass to 6.5 mm. It is this lesser diameter that is used in subsequent calculations. When mounted in the holder (illustrated as *M* in Fig. 1) the female portion of the standard taper was held against the male section with a steel spring. During the experiments, the tube containing the sintered glass plug was kept immersed in a water thermostat held at the desired temperature ± 0.1°C.

2. *Measurement of Flow Rates*

Fig. 1 illustrates the apparatus in which the flow rates of gases through the glass plug were measured. Its operation is as follows:

The gas under investigation is introduced into bulb *A* and burette *K* at pressure P_A and into bulb *B* at pressure P_B. The gas can be admitted either through the manifold above the bulbs, or through the ground glass joints on the sides. Bulbs *A* and *B* were insulated against sudden changes of temperature with a coating of asbestos–magnesia mixture.

The platinum contacts sealed through the wall of the manometer, *L*, are spaced 25 mm. apart. In each run P_A is chosen of such value that the mercury in the low arm of the manometer just touches a platinum contact. Each contact on the manometer, *L*, is wired to a separate terminal on the selector switch, *C*, with the contact on the bottom of the manometer forming a common terminal for all the circuits. When the desired pressures P_A and P_B have been set manually, the selector switch is adjusted to the contact number corresponding to pressure P_A. A potential exists between the platinum contact at the mercury meniscus and the one at the base of the manometer, such that when the circuit is closed, a current of 7 μamp. flows into the amplifier relay, *D*. When the pressure of the gas in bulb *A* and burette *K* falls below the desired value, the mercury in the low arm of the manometer closes the electrical circuit. The small current passing through the mercury

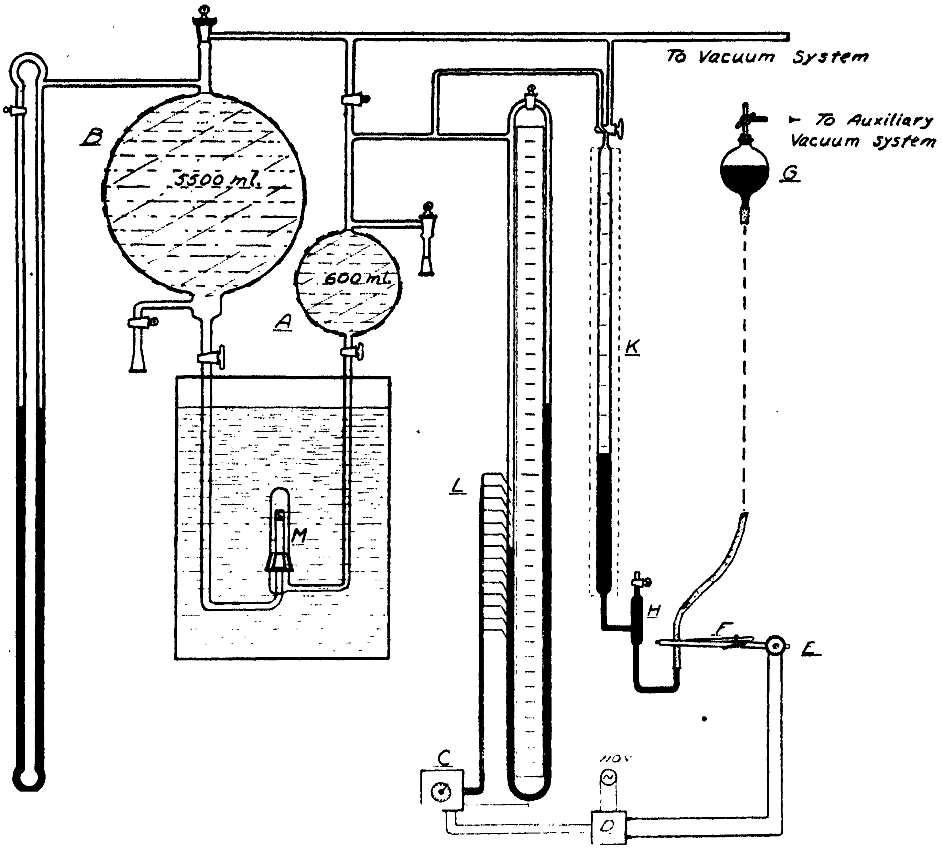

FIG. 1. *Apparatus for measuring flow of gases through porous glass plug.*

column is amplified and relayed in *D*, causing 5 amp. to flow through the solenoid, *E*. The solenoid then pulls open a pinchclamp, *F*, against the action of a spring, allowing mercury to flow from the reservoir, *G*, into the gas burette, *K*, thus restoring the pressure.

This manostatic control holds the pressure P_A constant to ± 0.2 mm. P_B is maintained manually; this is not difficult because of the large volume of bulb *B*. Exact pressures were read by means of a Gaertner cathetometer. By timing the rise of mercury in the burette, the rate of passage of gas through the sintered glass plug is obtained.

For all the experiments involving ethyl ether and ethyl bromide, the ground glass surfaces in the system were lubricated with a lubricant resistant to organic solvents (7).

3. *Apparatus for Ascertaining Interstitial Volume*

It was desirable to know what percentage of the spatial volume of the glass lattice is composed of micro pores between the glass particles. By micro pores, holes having a diameter of the order of 3×10^{-4} cm. and smaller are indicated. Pure mercury at 25°C. and 1 atm. pressure will not enter voids of microscopic or colloidal dimensions (5, p. 80). The over-all volume of the glass lattice was therefore obtained by means of the apparatus illustrated in Fig. 2.

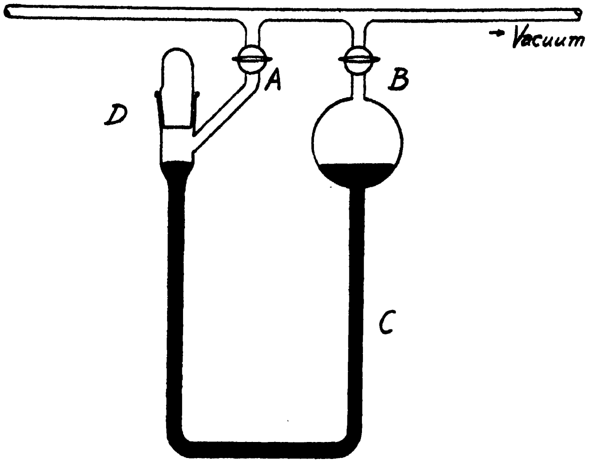

FIG. 2. *Apparatus for the determination of apparent density by mercury displacement.*

The operation of the apparatus is as follows. The illustration shows the level of the mercury in the apparatus with 1 atm. pressure in each tube. With taps *A* and *B* open, the space above the mercury is thoroughly evacuated. Tap *A* is closed, and air at 1 atm. pressure admitted through tap *B*; this forces the mercury to completely fill volume *D*. When *D* is completely filled, the mercury in the microburette *C* (5 ml. burette, graduated to 0.02 ml.) gives a reading near the bottom of the scale. Atmospheric pressure is then restored at *A* and *B* and the sample is introduced into volume *D* by way of the cap. The mercury is then forced under 1 atm. pressure to fill volume *D* as before, and a second reading taken on the burette tube. The difference between readings is the volume of the glass plus the micro pore volume. From the weight of the plug and the accurately known specific gravity of Pyrex, the actual volume occupied by the glass in the plug is readily obtained and the micro pore volume calculated.

4. *Measurement of the Ether Adsorption Isotherm of the Glass Plug*

The isotherm measurements were made on a McBain–Bakr (6) balance, a long and sensitive quartz fibre being employed and the extension of the spiral being observed through a 40-power microscope with a calibrated eyepiece scale. The spiral had a sensitivity of 0.54 mm. per mgm. load, and the microscope magnified the movement to 0.046 mgm. per scale division.

5. *The Gases*

The gases and vapours used in these experiments are listed below, together with their viscosities at 35°C., their molecular weights, and their source.

The three permanent gases were admitted to the system through liquid air traps to remove any condensable impurities. Except for this precaution,

Gas or vapour	Viscosity at 35°C., micropoises	Molecular wt.	Source
Helium (4)	202.5	4.003	U.S. Govt. Cylinder
Hydrogen (12)	90.3	2.016	Ohio Cylinder Gas Co.
Nitrogen (12)	181.5	28.016	Dom. Oxygen Company
Diethyl ether (10, 11)	77.4	74.12	Merck Reagent Chemical (distilled from sodium)
Ethyl bromide (9, 11)	180.0	108.98	Baker and Adamson, Reagent Chemical

the gases were used as received in the laboratory, without any attempt at additional purification. The nitrogen was analysed for oxygen prior to its use; the oxygen content was 0.2%. Since the hydrogen was made electrolytically, it was presumed to be quite pure. The helium, however, probably contained a trace of impurity, which changed its viscosity slightly, for the data obtained in the helium experiments were not quite consistent with those of the other two gases. This particular selection of materials was made so as to provide a range of molecular weights, viscosities, and boiling points.

(B) Experimental Results

The flow rate measurements were made on the apparatus illustrated in Fig. 1, using a 50 mm. pressure gradient across the plug, at mean pressures varying from 25 to 675 mm. in 50 mm. steps. All the data listed were obtained by measuring the gas flow over a 30-min. period. This fact is important when regarding the hysteresis effects observed with the condensable vapours. Unless otherwise stated, the temperature was 35°C. ± 0.1°C. during all the runs.

The numerical results are listed in Table I and are represented graphically in Figs. 3 and 4.

The lines in Fig. 3 have all been calculated to the best fit of the data by the method of least squares.

It is now proposed to apply conventional flow equations to the experimental data obtained.

The two common equations expressing the mechanism of gaseous transfer in cylindrical tubes are Poiseuille's equation for streamline flow, and Knudsen's equation for molecular streaming.

Poiseuille's equation

$$\frac{dn}{dt} = \frac{r^4\pi\bar{P}(P_A-P_B)}{8l\eta RT}$$

describes the flow occurring in a tube whose diameter is large compared to the mean free path of the gas molecules. It is therefore the flow equation describing gas transfer at high pressures. In its simplest form, it may be written

$$\frac{dn}{dt} = \frac{a\bar{P}\ (P_A - P_B)}{\eta},$$

TABLE I

FLOW RATE OF GASES THROUGH SINTERED GLASS PLUG

$\bar{P}$, or $\frac{P_A+P_B}{2}$, mm.	Volume passing per minute, in ml. calculated to S.T.P.				
	Ethyl ether	Ethyl bromide	Helium	Hydrogen	Nitrogen
26.0	0.08	0.091	0.380	0.550	0.157
76.0	0.154	0.141	0.392	0.60	0.183
125.5	0.244	0.207	0.44	0.67	0.22
174.0	0.341	0.245	0.495	0.73	0.24
223.0	0.47		0.50	0.78	0.28
273.1	0.490	0.376	0.52	0.85	
322.0		0.381	0.55	0.895	0.34
370.7	0.64	0.391	0.60	0.955	0.34
421.3	0.66		0.60	0.985	0.37
468.8			0.64	1.04	0.41
518.0			0.64	1.09	0.42
566.9			0.68	1.14	
615.4			0.71	1.16	
669.8			0.72		

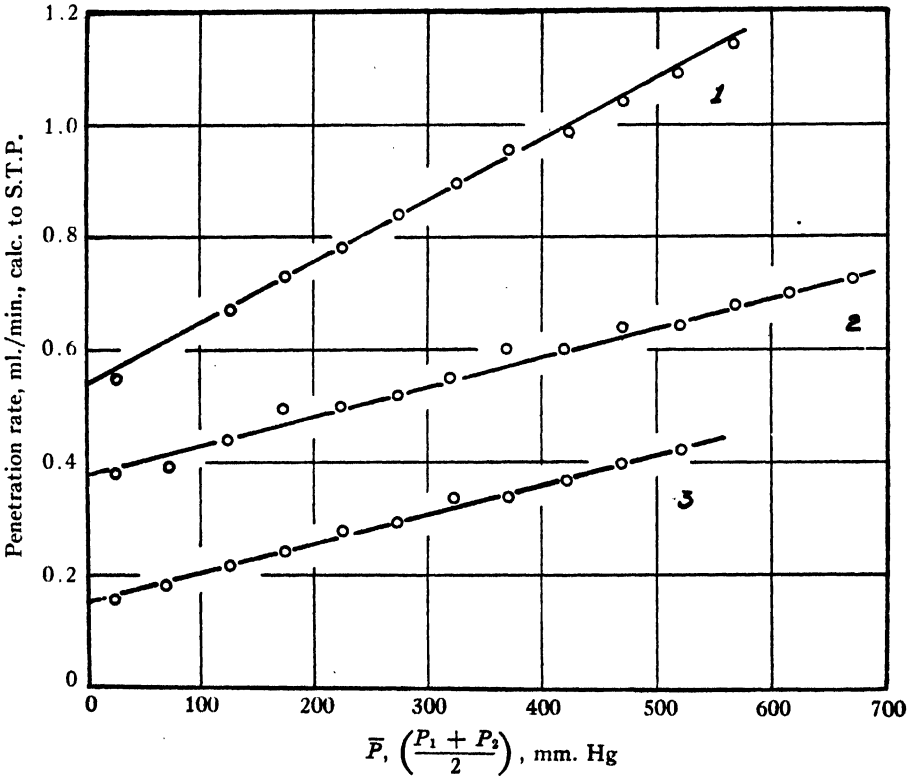

FIG. 3. *Rate of flow of permanent gases through porous glass plug. Curve 1—hydrogen; Curve 2—helium; Curve 3—nitrogen.*

showing the dependence of flow rate directly on the mean pressure and inversely on the viscosity.

Knudsen's equation expresses the condition of gas transfer when the mean free path is large compared with the tube diameter, and is thus the equation holding for low pressures.

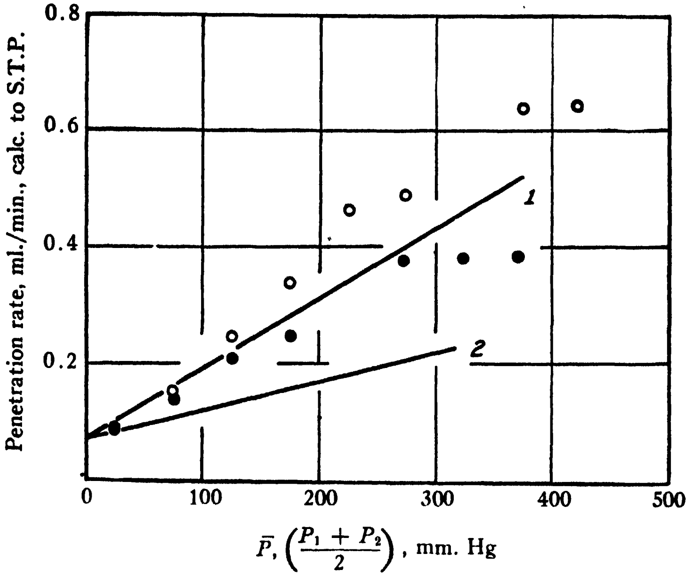

FIG. 4. *Rate of flow of vapours through porous glass plug.* ○—*Experimental values for diethyl ether.* ●—*Experimental values for ethyl bromide. Curve 1—Diethyl ether as predicted by Knudsen–Poiseuille flow. Curve 2—Ethyl bromide as predicted by Knudsen–Poiseuille flow.*

The equation is:

$$\frac{dn}{dt} = \frac{4}{3}\,\frac{r^3\sqrt{2\pi}(P_A - P_B)}{l\sqrt{MRT}},$$

and can be simplified to

$$\frac{dn}{dt} = \frac{B(P_A - P_B)}{\sqrt{M}}.$$

The flow-rate is thus independent of the mean pressure and proportional to $\frac{1}{\sqrt{M}}$.

Bearing these two equations in mind, it is apparent that somewhere along the pressure scale, Knudsen flow will give way to Poiseuille flow, and, at the point of change-over, the flow rate will cease to be proportional to $\frac{1}{\sqrt{M}}$, and will become proportional to $\frac{1}{\eta}$. H. Adzumi (1, 2), in his experiments on the diffusion of permanent gases through earthenware plates, found that the above two types of flow did overlap, and he combined the two equations into one, taking into account an added factor, γ, the coefficient of slip.

His modification of the flow equations is

$$\frac{dn}{dt} = \frac{\pi}{8\eta RT} \cdot \frac{\bar{P}N\bar{r}^4}{l}(P_A - P_B) + \gamma\frac{4}{3} \cdot \frac{\sqrt{2\pi}}{\sqrt{MRT}} \cdot \frac{N\bar{r}^3(P_A - P_B)}{l} .$$

This may be simplified to

$$G = \frac{\pi}{8\eta RT} \cdot \frac{\bar{P}N\bar{r}^4}{l} + \gamma\frac{4}{3}\frac{\sqrt{2\pi}}{\sqrt{MRT}} \cdot \frac{N\bar{r}^3}{l},$$

where G = flow rate per unit time per unit pressure gradient,

N = number of pores in the plug in question,

$\bar{P}$ = mean pressure $= \dfrac{P_A + P_B}{2}$,

$\bar{r}$ = effective average pore radius,

l = " " " length,

η = gaseous viscosity,

γ = coefficient of slip, and, where there is no specular reflection of gas molecules from the pore walls, may be evaluated as 1.0. For the pressure range in question, γ was taken as 0.9.

M = molecular weight of gas.

The above equation is the equation of a straight line representing the variation of the flow rate through the glass plug as a function of the mean pressure. The slope of the G vs. $\bar{P}$ curve gives the value of $\dfrac{\pi}{8\eta RT} \cdot \dfrac{N\bar{r}^4}{l}$, and the intercept on the G-axis evaluates $\dfrac{4}{3} \cdot \dfrac{\sqrt{2\pi}}{\sqrt{MRT}} \cdot \dfrac{N\bar{r}^3}{l}$. Dividing the former by the latter gives the value of $\bar{r}$.

For the permanent gases straight lines were obtained when the rate of flow was plotted against the mean pressure as seen from Fig. 3. The values of $\bar{r}$ from these curves are $1.34\,\mu$, $1.16\,\mu$, and $1.16\,\mu$ for helium, hydrogen, and nitrogen respectively. Using an average value of $1.2\,\mu$ the number of pores was calculated to be 3×10^5 in the plug in question.

With the condensable vapours (see Fig. 4) not only does a falling-off of rate occur at about 50% saturation pressure, but the data at lower pressures do not fit a straight line. However, if the line of best fit is drawn through these points, values of $\bar{r}$ calculated are $3.6\,\mu$ and $3.2\,\mu$ for ethyl ether and ethyl bromide, while the values of N were 1×10^4 and 2.5×10^4. It is therefore concluded that the behaviour of the condensable vapours is not in accordance with the Poiseuille–Knudsen equation. The straight lines appearing in Fig. 4 represent the behaviour of the condensable vapours, assuming that their behaviour corresponded with that of the three permanent gases. It is apparent that, at the very low pressures, the experimental data conform with this assumption. As the pressure increases, the flow rates of the vapours are higher than those predicted by Poiseuille–Knudsen flow up to the point where the falling-off occurs.

Now, since the glass plug was made from glass particles of mean diameter 12 μ, it would be of interest to see whether the pore size as obtained from the flow equations is of the same order of magnitude as the average pore size calculated from the geometry of the packing in the plug. To make this calculation, an estimate was necessary of the type of packing that existed in the plug after sintering. Since the percentage of voids in the lattice is some indication of the arrangement of the particles, a mercury density measurement was made on a portion of the plug, using the apparatus described above. The lattice was found to be composed of 24.4% voids, which corresponds fairly well with the figure for closest packing of spheres (25.95%)(3). Assuming, then, that the arrangement of the particles in the plug approximates the rhombohedral packing of spheres, the mean pore radius was calculated by the method of W. O. Smith (8). The figure calculated for the mean pore radius by this method was 1.7 μ, in good agreement with the flow radius of 1.2 μ for the permanent gases. Assuming the same arrangement, the number of pores per square centimetre for 12 μ spheres is 8×10^5 as compared to 9.9×10^5 calculated from the flow equation.

As can be seen from Fig. 4, for both ethyl ether and ethyl bromide, a falling-off of flow rate was observed, considerably below the saturation pressure for each vapour. At 35°C. the falling-off occurs at about 275 mm. for ethyl bromide and about 375 mm. for ether vapour. Further investigations brought out the following observations:

(*a*) The penetration rate of a condensable vapour through the porous glass plug at a pressure exceeding 60% of the saturation pressure decreased to an equilibrium value after the plug had been exposed to the vapour for a sufficiently long time. The rate reached at equilibrium was always of the order of 90% of the rate obtained by extrapolation of the first part of the G vs P curve.

(*b*) The values for G, obtained from 30-min. runs with ether vapour at 25°C., were true equilibrium values only up to about 160 mm. pressure, and the equilibrium values in every case above 160 mm. were lower than those obtained from a 30-min. run.

(*c*) After the glass plug had been equilibrated for 18 hr. to ether vapour at 25°C. and 446 mm., the pressure was lowered and a diffusion rate measurement was carried out immediately at a mean pressure of 126 mm. The rate obtained on a 30-min. run under these conditions was considerably lower than that observed when measurements were made directly, without previous equilibration. However, the rate continued to increase throughout the 30-min. period. On letting the plug stand for five hours at 126 mm., a new diffusion rate measurement showed a return to the original value. This experiment demonstrated the hysteresis.

The McBain–Bakr balance was used to determine whether any measurable amount of ether was adsorbed at the pressures at which the flow experiments were carried out. The measurements were made at 25° C. using two sections cut from the glass plug, weighing 0.4428 and 0.3546 gm. In no case was any adsorption detected below 92% saturation pressure. With a glass fragment weighing 0.4428 gm., 0.07 mgm. was adsorbed after one hour at an ether pressure of 493 mm. Below this pressure, in the region where the flow experiments were made, the ether adsorbed could not be detected with the apparatus used.

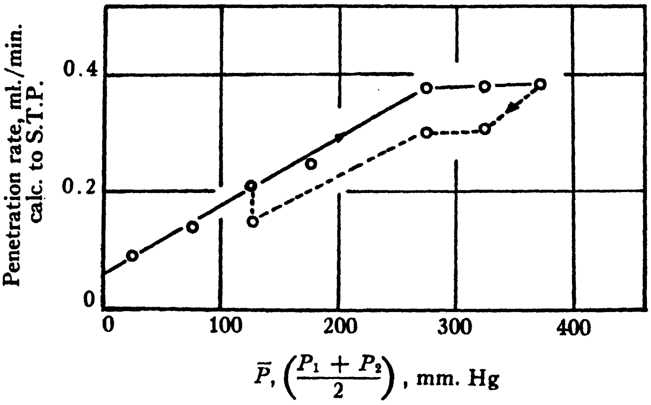

FIG. 5. *Hysteresis effect as observed for ethyl bromide flow through sintered glass plug.*

Discussion

The permanent gases, when flowing through the sintered glass plug, are transferred by a combination of Knudsen and Poiseuille flow, consistent with gaseous flow through fine capillaries. The average effective pore radius of 1.2 μ determined for the permanent gases agrees well with the value of the average radius of the interstices between closest packed 12 μ spheres.

Two anomalies are exhibited in the transfer of condensable vapours through the sintered glass plug. First, the flow rate begins to fall off rather suddenly at a relative pressure of about 50% of the saturation pressure, hysteresis being also observed in this region. Second, below this pressure the rate of transfer is higher than that predicted by Poiseuille–Knudsen flow, the divergence increasing as the pressure increases.

The latter of these phenomena suggests that some other method of transfer exists in addition to ordinary gaseous flow. This may be the flow along the surfaces of an adsorbed layer, which no doubt exists on the glass although the sensitivity of the adsorption apparatus used could detect no adsorption at the lower pressures.

The falling-off of flow rate of the vapours at a fraction of the saturation pressure, and particularly the hysteresis associated with it, suggests that this phenomena is caused by physical adsorption or condensation. The medium is composed of packed granules and the spaces between are a series of fairly large voids interconnected by narrow necks and not a bundle of parallel capillaries as assumed by Adzumi. If we assume that at the points of constriction where the actual radius is very much less than 1.2 μ, some capillary condensation occurs, blocking a sufficient number of paths to reduce the flow rate by the amount observed, we have a mechanism explaining the phenomena. The quantity of material necessary for this effect could be very small and escape detection in the adsorption apparatus. This view is strongly supported by the hysteresis effects, which are difficult to explain in any other way.

The following conclusions are drawn from the investigation:

(i) For the flow of permanent gases, a sintered glass plug may be regarded as a bundle of parallel capillaries, and the conventional treatment gives satisfactory results.

(ii) A porous medium, even as inert as glass, cannot be correctly regarded as a system of parallel cylinders when a mathematical treatment is employed to describe the transfer of condensable vapours. The evidence of surface flow and the blocking-off and hysteresis effects invalidate the simple picture in this case.

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INSTABILITY OF SOLUTIONS OF HIGH POLYMERS[1]

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Abstract

The change in the viscosity property of solutions of high polymers on ageing has been investigated. It has been found that the variations in viscosity are due to changes in the molecular weight of the dissolved polymer, caused by the presence of small amounts of impurities. In particular, oxygen appears to give rise to degradation reactions, while iron salts cause the formation of gel structures. Solutions of the dry polymers in pure solvents, when aged in the absence of air, show only very small variations in viscosity. The investigation has been conducted with three polymers, polyvinyl acetate, polystyrene, and polymethyl methacrylate in solution in three solvents, bis(2-chloroethyl) ether, nitrobenzene, and bis(2-chloroethyl) sulphide.

The principal reaction seems to occur between the impurity and the polymer, with the solvent acting as an inert medium. However, it appears that in the case of bis(2-chloroethyl) sulphide, reaction of iron salts with the solvent is possible.

The intrinsic viscosity of polyvinyl acetate recovered from the aged solutions has been determined. The k' factor of Huggins has been evaluated from these measurements, and appears to change during some of the ageing processes.

Introduction

Several instances of instability in solutions of high polymers are recorded in the literature, and have been observed generally as changes in the viscosity property. Mead and Fuoss (4) report viscosity instability for solutions of polyvinyl chloride in methyl amyl ketone and cyclohexanone, and attribute the changes in viscosity to the untangling and elongating of the polymer chains. Wehr (9) states that the stability of solutions of polyvinyl chloride in several solvents depends upon the degree of saturation of the polymer, the light intensity, and the presence of acids, bases, and catalysts. Blaikie and Crozier (2) aged solutions of polyvinyl acetate in glacial acetic acid in glass bombs at 160° C., and observed an initial decrease in the viscosity, followed by an increase at the end of four weeks, the changes being smaller when air was excluded.

Bartell and Cowling (1) found that the introduction of various metals as salts into alkali cellulose altered the rate of lowering of viscose viscosity with length of time of ageing the alkali cellulose. Manganese (and iron to a lesser extent) increased the rate of change of viscosity by increasing the rate of

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depolymerization of the cellulose by oxygen. Further evidence of the effect of oxygen comes from the work of Naunton (6) on rubber photogels. When solutions containing rubber were exposed to light in the presence of an excess of oxygen, the oxygen was absorbed slowly and the viscosity of the solutions decreased to a limiting value. While the type of degradation was similar in all solutions, the extent of the change was dependent partly upon the solvent.

The present investigation arose through the necessity of storing solutions of high polymers in technical solvents for long periods in iron containers. For this reason, the effects of iron salts and of air were studied extensively. An ageing temperature of 60° C., which was thought to be the highest encountered in normal storage, was used throughout. The greater portion of the results was derived from systems containing polyvinyl acetate, which was of more practical interest to the investigation. The change in the viscosity property of the solutions was used as a measure of stability, which limits the expression of the results in a quantitative manner.

Experimental

Viscosity Measurements

Measurements were made with three types of viscometers. To measure the viscosity of the aged solutions, a U-tube capillary viscometer, developed at Porton, England, was used. Results could be reproduced to better than 1% with this instrument, which had the advantage that only a very small sample (about 0.5 cc.) was required. To detect the presence of gel structure, and to measure deviations from Newtonian flow properties in the polymer solutions, a modified Ubbelohde (8) suspended level viscometer was employed. From the dimensions of the instrument and from the Hagen–Poiseuille formula it was possible to derive values for the rate of shear and the shear stress to which the liquids were subjected. The presence of structure was indicated when a plot of the shear stress against the rate of shear showed an intercept on the shear stress axis. The intrinsic viscosity of polyvinyl acetate was derived from measurements in dilute solution in acetone, using the conventional Ostwald viscometer. The data were plotted in the form $\frac{\ln \eta_r}{c}$ versus c, where η_r = relative viscosity and c = concentration in grams per 100 cc. of solution. Extrapolation to zero concentration gave the intrinsic viscosity. The k' factor was derived from the relation of Huggins (3) $k' = \frac{1}{2} - \frac{\text{slope}}{[\eta]^2}$.

All viscosity measurements were made at 20° C.

Materials

Three types of polymers were studied:

Polyvinyl acetate (Gelva V-45, Shawinigan Chemicals Ltd.).

Polymethyl methacrylate (NDR-359, E. I. duPont de Nemours).

Polystyrene (Styron A-200, Dow Chemical Co.).

The polymers were dried for 48 hr. *in vacuo* before being dispersed in the solvents. Insoluble material was removed by filtering the viscous solutions rapidly through a mat of glass wool. The saponification values of samples of polyvinyl acetate were determined by the method of Minsk *et al.* (5).

The solvents, with the exception of bis(2-chloroethyl) sulphide, were obtained by distilling the technical materials *in vacuo*. Bis(2-chloroethyl) sulphide was prepared by the reaction of concentrated hydrochloric acid with thiodiglycol, with subsequent distillation *in vacuo*. The purified solvents were stored over "Drierite."

Anhydrous ferric chloride was prepared by passing a stream of dry chlorine diluted with nitrogen over iron powder heated to a dull red in a Pyrex tube. The shiny black crystals of ferric chloride were collected from the cool part of the tube, and were stored in a vacuum desiccator. Analysis showed the material to be 99% pure. Anhydrous ferrous chloride was prepared in a similar manner by using dry hydrochloric acid gas, and by analysis was 98% pure.

Ageing Procedure

Throughout the investigation an effort was made to keep the systems free from moisture. The viscous solutions were prepared in closed vessels equipped with mercury seal stirrers. In preparing the solutions containing varying concentrations of iron, the salt was added quickly to a weighed portion of the solvent. This solution was diluted with a measured quantity of polymer solution to give a desired concentration of iron salt.

For the most part, the viscous solutions were aged in sealed glass bombs. A few comparative experiments were performed using glass stoppered bottles as containers. The bombs were equipped with two side-arms and a stirrer consisting of a nail sealed within a piece of glass tubing. Each bomb was filled with approximately 100 cc. of viscous solution through one of the side-arms. This arm was sealed off, and the other was connected through a ground glass joint to a vacuum line operating at a pressure of 0.005 mm. of mercury. The solution was degassed with stirring until the pressure was equal to the vapour pressure of the solvent. In any one series of experiments, the time of evacuation for each bomb was kept constant, so that solvent losses were the same in each case. The bombs were sealed off under vacuum, and set to age in a large air-bath controlled to 60 ± 0.1° C. At appropriate intervals bombs were removed from the bath, and cut open, after which the viscosity of each solution was measured. In the case of the polyvinyl acetate series the polymer was recovered and compared with the original material on the basis of intrinsic viscosity and in some cases on the basis of saponification value.

Two methods of recovering the polyvinyl acetate were tried. The first of these consisted of steam distilling the solutions of polyvinyl acetate in bis(2-chloroethyl ether), but it was found that the process hydrolysed part of the polymer, as shown by low and irregular saponification values and yields. This may have been caused by hydrochloric acid from hydrolysis of the solvent. A second method, using organic precipitants, proved to be quite satisfactory. The viscous solution was poured slowly into an excess (6 : 1 by volume) of petroleum ether (30° to 60° C. fraction) which was stirred violently. The precipitated polymer was dissolved in benzene (100 cc. per 8 gm. of polymer) and again brought down in petroleum ether under similar conditions. Excess solvent was drawn off under vacuum, after which the polymer was dissolved in acetone (100 cc. per 8 gm. of polymer), and precipitated in a large excess of water. The porous mass was dried to constant weight *in vacuo*, and cut into small pieces. The yield was generally within 2% of the theoretical, and the saponification value was unchanged by the process.

Results

The experimental data may be divided into two sections. The first deals with the system polyvinyl acetate–bis(2-chloroethyl) ether, while the second is concerned with the extension of the investigation to the other polymer–solvent systems.

A. Initially, solutions of Gelva V-45 in pure bis(2-chloroethyl) ether were aged at 60° C. in sealed bombs in the absence of air. The data for two such series are given in Tables I and II. In Table II, the polymer viscosity denotes the viscosity of a standard solution of the polymer in benzene (86 gm. per litre of solution).

In both series (Tables I and II) the changes in viscosity are small. In Table I the upward trend in viscosity is followed by a similar trend in the

TABLE I

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises	% Recovery of polymer	Intrinsic viscosity	k'
0	5.55	99.5	1.05	0.37
14	5.70	99.0	1.12	0.33
28	5.70	98.0	1.11	0.33
60	5.75	100.0	1.09	0.35
104	5.85	98.5	1.13	0.35
188	5.90	—	1.12	0.35

TABLE II

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises	% Recovery of polymer	Polymer viscosity, centipoises	Saponification value, %
0	4.90	99.5	52.9	98.5
8	4.55	100.0	48.2	99.5
19	4.65	98.5	51.2	96.5
54	4.75	97.0	54.5	97.0

intrinsic viscosity of the recovered polymer within experimental error. The k' value also changes during the ageing process, but the variation is hardly consistent enough to be significant. In Table II the change in viscosity of the thickened solutions is followed by a similar change in the polymer viscosity. At the same time the saponification values vary, but in an irregular manner. This can probably be attributed to the method of determination.

For comparison, in Table III are shown data for similar solutions aged in bombs of which only the headspaces were evacuated, and in glass stoppered bottles.

TABLE III

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises	
	Bombs	Glass bottles
0	3.70	3.80
11	3.05	2.20
25	3.00	1.40
30	2.95	—
74	—	0.30

A decrease in viscosity is observed for both types of storage, the change being greater in the glass bottles. In conjunction with the data in Tables I and II, three ageing conditions are represented; absence of air, limited amount of air, and unlimited amount of air. The results indicate then that the polymer solutions are degraded only when air is present. The materials were dried before the preparation of the thickened solutions; this seems to eliminate the possibility that the effect is caused by water vapour. Oxygen appears then to be the degrading agent, in agreement with the findings of other workers (1, 2). Preliminary experiments on the ageing of solid polyvinyl acetate in an atmosphere of oxygen indicate that the polymer is degraded (10).

A large sample of a solution of Gelva V-45 in bis(2-chloroethyl) ether was aged in a stoppered flask at 60° C. At intervals the polymer was separated from small portions of the solution, after which the intrinsic viscosity of the polymer was measured. The data are shown in Table IV.

TABLE IV

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises	Intrinsic viscosity	k'
0	3.70	1.07	0.34
8	3.50	1.03	0.34
87	3.25	0.98	0.36
154	3.15	0.95	0.33

The change in viscosity is not as large as that shown in the second column of Table III. This is probably due to the fact that the flask was nearly filled with liquid, and as a result the ratio of the volume of air to the volume of liquid was small compared with that existing in glass stoppered bottles. The important point is that the change in viscosity is paralleled by a similar change

TABLE V

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER PLUS 0.003% FERRIC CHLORIDE

Ageing time, days	Viscosity, poises	Intrinsic viscosity	k'
0	3.55	1.01	0.34
1	5.45	1.24	0.37
2½	8.70	1.59	0.38
3	12.0	1.66	0.39
5	13.3	1.72	0.39

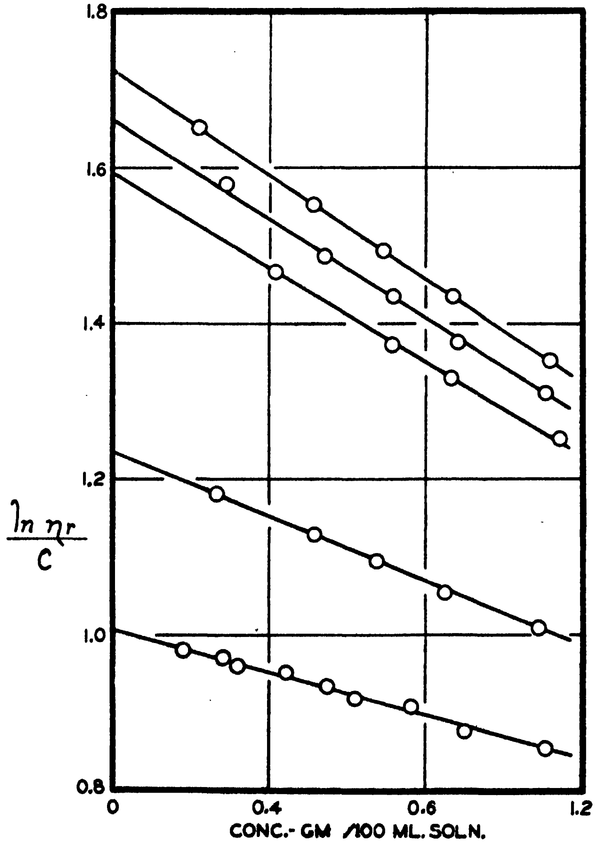

FIG. 1. *Determination of intrinsic viscosity of polyvinyl acetate in acetone.* $[\eta] = \lim_{c \to 0} \frac{\ln \eta_r}{c}$

in the intrinsic viscosity of the recovered polymer. This suggests that the molecular weight of the polymer is lowered in the ageing process. The *k′* value has changed during ageing but again the change is irregular and may not be significant.

The effect of iron salts was noted first when approximately 0.25% of ferric chloride was added to a solution of Gelva V-45 in bis(2-chloroethyl) ether and caused the formation of a gel. Many such experiments were performed but it will suffice to set down typical results. In Table V data are recorded for a series of solutions containing 0.003% of anhydrous ferric chloride, which were sealed in bombs at a pressure of 0.1 mm. of mercury.

A threefold increase in viscosity is paralleled by a large increase in the intrinsic viscosity of the recovered polymer. This again suggests that the change in the original solution on ageing is due to a change in the molecular weight of the dissolved polymer. These data are plotted in Figs. 1 and 2.

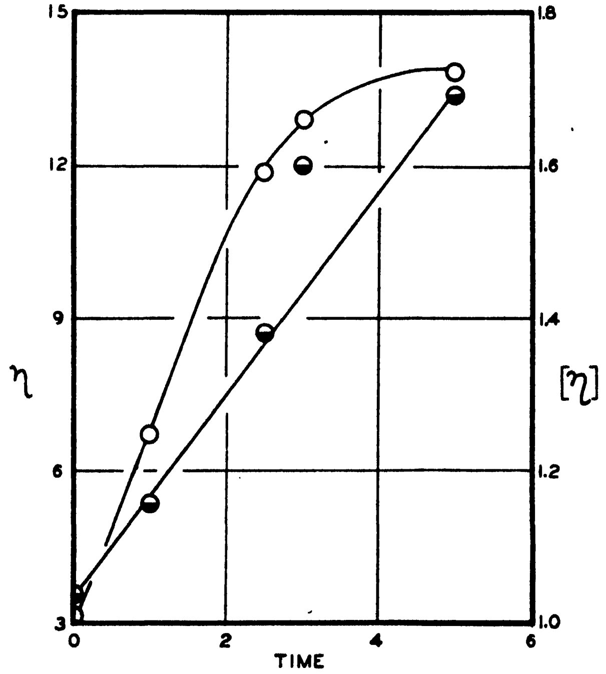

FIG. 2. ◒——◒ *change of viscosity of solutions of Gelva V-45 in bis(2-chloroethyl) ether plus 0.003% ferric chloride on ageing.*

○——○ *change of intrinsic viscosity of the recovered polyvinyl acetate.*

The *k′* value shows an upward trend which may be construed as a change in the average shape or configuration of the polymer. It is of interest to compare the intrinsic viscosity and *k′* of a higher molecular weight polyvinyl acetate, Gelva V-150, with those in Table V. The $[\eta]$ and *k′* of Gelva V-150 are 1.82 and 0.37 respectively, which are not very different from the values for the last sample in Table V. This supports the view that the change in intrinsic viscosity represents a change in molecular weight.

When solutions of Gelva V-45 in bis(2-chloroethyl) ether containing more than 0.005% of ferric chloride were sealed in evacuated glass bombs, only a viscosity increase was observed, while in glass bottles a decrease in viscosity was observed first. In either case, the end result was a firm gel. This is illustrated by the data in Table VI.

TABLE VI

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER

Ageing time, days	Viscosity, poises		
	Plus 0.1% $FeCl_3$ in bombs	Plus 0.01% $FeCl_3$ in bottles	Plus 0.1% $FeCl_2$ in bottles
0	7.3	4.1	5.0
½	10.3	—	—
1	Gel	—	—
4	—	—	4.5
12	—	2.3	1.9
23	—	2.6	2.7
28	—	—	Gel
31	—	4.5	—
36	—	4.6	—
38	—	Gel	—

The viscosities of these solutions were measured in the Ubbelohde viscometer, and it was observed that deviations from Newtonian flow were obtained only when the viscosity was increasing. This is shown in Fig. 3, where the data from the third column of Table VI are plotted. An intercept on the shear stress axis first appears with the third sample. Within the limit that this method can detect structure, it appears that the degradation and the gel forming reactions are independent of each other.

In the presence of air, ferrous chloride caused effects similar to those of ferric chloride (Column 4, Table VI). This is undoubtedly due to the oxidation of the ferrous salt to the ferric form by air. In evacuated bombs, ferrous chloride caused a gradual increase in viscosity, as is shown in Table VII. Many similar solutions aged in evacuated bombs were aged for periods up to six months without appearance of gel structures, in clear contrast to the behaviour with ferric chloride.

The polymer viscosity increases in keeping with the increase in the viscosity of the original solution. This is a behaviour similar to the change in intrinsic viscosity shown in Table V. At the same time, the change in saponification value is small and irregular. What change does occur is probably within the limit of accuracy of the saponification method. The change in viscosity cannot then be due to a hydrolytic reaction.

TABLE VII

THE AGEING OF GELVA V-45 IN BIS(2-CHLOROETHYL) ETHER PLUS 0.1% FERROUS CHLORIDE

Ageing time, days	Viscosity, poises	% Recovery of polymer	Polymer viscosity, centipoises	Saponification value, %
0	5.20	100.0	51.0	98.5
7	6.05	98.5	62.5	98.0
20	6.60	96.5	67.1	98.0
32	6.95	98.0	69.7	97.0

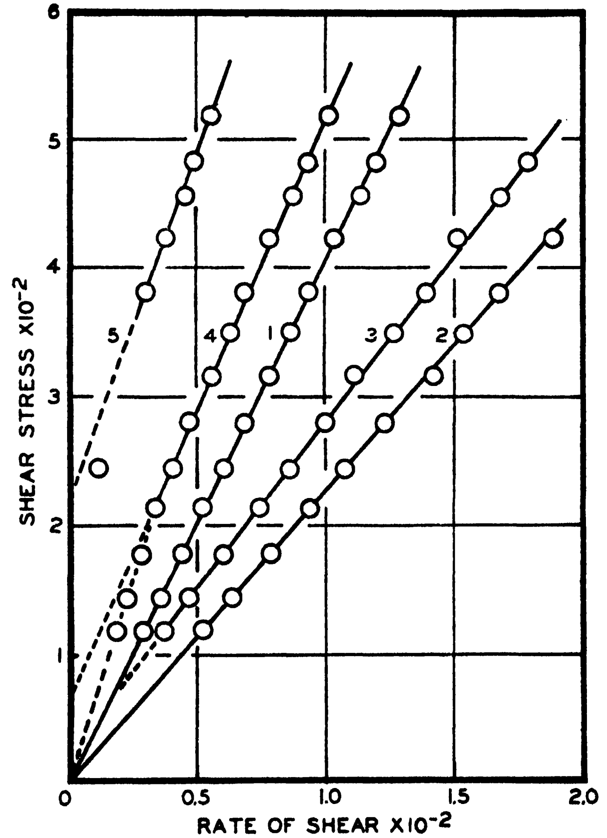

FIG. 3. *Typical plot of shear stress against rate of shear derived from viscosity measurement with the Ubbelohde viscometer.*

B. To test the generality of viscosity instability, solutions of the three polymers in three solvents were prepared. To these solutions were added various concentrations of ferric or ferrous chloride, and samples of each solution were aged both in evacuated bombs and in glass stoppered bottles. The viscosity of the solutions in the bottles was measured at intervals, while for the bombs, only the time of gel formation was recorded. The data are summarized in Table VIII.

TABLE VIII

THE AGEING OF SOLUTIONS OF GELVA V-45, STYRON A-200, AND NDR-359 IN BIS(2-CHLOROETHYL) ETHER, IN NITROBENZENE AND IN BIS(2-CHLOROETHYL) SULPHIDE

Solvent	% Iron salt	Bottles		Bombs
		Initial viscosity	Final viscosity	
(a) 10% Gelva V-45				
Bis(2-chlorethyl) ether	Ferric			
	0.1	3.6	Gel 5 days	Gel 2 days
	0.01	3.3	Gel 38 days	Gel 4 days
	0.001	3.5	0.5 170 days	No gel 163 days
	0.0	3.5	0.5 170 days	—
	Ferrous			
	0.1	3.5	Gel 13 days	No gel 150 days
	0.01	3.5	Gel 22 days	No gel 150 days
	0.001	3.5	0.1 140 days	No gel 150 days
	0.0	3.5	0.5 140 days	—
Nitrobenzene	Ferric			
	0.25	—	Gel 12 hr.	—
	0.1	3.0	Gel 1 day	Gel 2 hr.
	0.01	4.4	Gel 2 days	Gel 13 hr.
	0.001	2.8	No gel 120 days	—
Bis(2-chloroethyl) sulphide	Ferric			
	1.0	—	Gel 1 day	Gel 1 day
	0.3	7.1	8.0 190 days	Gel 60 days
	0.1	6.6	8.5 190 days	Gel 82 days
	0.01	6.9	6.8 190 days	Gel 121 days
	0.001	7.0	7.0 190 days	Gel 150 days
	0.0	7.0	7.0 190 days	—
	Ferrous			
	0.1	6.7	8.0 150 days	Gel 130 days
	0.01	6.7	7.0 150 days	Gel 130 days
	0.001	6.7	6.5 150 days	Gel 130 days
	0.0	6.6	6.7 150 days	—
(b) 7.5% Styron A-200				
Bis(2-chloroethyl) ether	Ferric			
	0.1	3.0	Gel 38 days	—
	0.01	3.0	Gel 22 days	Gel 36 days
	0.001	3.0	0.5 140 days	No gel 140 days
	0.0	3.0	0.5 140 days	No gel 140 days
Nitrobenzene	Ferric			
	0.1	1.6	2.0 160 days	No gel 160 days
	0.01	3.0	2.0 160 days	No gel 160 days
	0.001	3.1	3.0 160 days	No gel 160 days
	0.0	3.1	3.0 160 days	No gel 160 days

TABLE VIII—*Concluded*

THE AGEING OF SOLUTIONS OF GELVA V-45, STYRON A-200, AND NDR-359 IN BIS(2-CHLOROETHYL) ETHER, IN NITROBENZENE AND IN BIS(2-CHLOROETHYL) SULPHIDE—*Concluded*

Solvent	% Iron salt	Bottles		Bombs
		Initial viscosity	Final viscosity	
(c) 1% NDR-359				
Bis(2-chloroethyl) ether	Ferric			
	0.1	3.1	0.2 52 days	Gel 14 days
	0.01	12.0	0.4 52 days	No gel 175 days
	0.001	21.0	0.5 170 days	No gel 175 days
	0.0	20.0	0.5 170 days	—
Nitrobenzene	Ferric		Polymer	
	0.1	1.3	Sep. 104 days	Gel 16 days
	0.01	6.8	Stringy 175 days	No gel 175 days
	0.001	8.3	4.0 175 days	No gel 175 days
	0.0	9.7	5.0 175 days	No gel 175 days
Bis(2-chloroethyl) sulphide	Ferric			
	0.1	3.8	3.0 110 days	No gel 110 days
	0.01	10.3	4.0 110 days	No gel 110 days
	0.001	10.6	4.0 110 days	No gel 110 days
	0.0	11.5	4.5 110 days	No gel 110 days

For Gelva V-45 in bis(2-chloroethyl) ether and in nitrobenzene, concentrations of 0.01% or greater of ferric chloride cause gel formation. Similar solutions containing ferrous chloride and aged in bottles behave similarly. With bis(2-chloroethyl) sulphide as solvent the concentration of ferric chloride that will produce gels in solutions aged in the presence of air is of the order of 1%. At the same time, as little as 0.001% of either ferrous or ferric chloride causes gel formation in evacuated bombs.

Somewhat similar effects are noted in Parts (*b*) and (*c*) of Table VIII. Concentrations of ferric chloride of 0.01% or greater cause gel formation in solutions of Styron A-200 in bis(2-chloroethyl) ether. Little effect is observed in the solutions of Styron in nitrobenzene. This may be due in part to strong attraction between the polymer and the solvent, both being aromatic in character.

The failure of NDR-359 to form gels as readily as the other two polymers is due possibly to the low concentration of this material used. In some of the experiments the polymer appeared to separate out on ageing, leaving a solution of very low viscosity.

Whether a particular solution takes on gel characteristics or not appears to depend upon the degree of solvation of the polymer by the solvent. In non-solvating solvents, gels are not to be expected. For example, a solution of Gelva V-45 in acetone containing 0.25% of ferric chloride was aged for 26 days at 60° C. in a sealed bomb. During this time, the viscosity increased from 17 to 21 centipoises. The polymer, after being recovered from the solution, was only partially soluble in benzene.

A similar solution with toluene as solvent was aged for 3½ months at 60° C. The viscosity as measured in the Ubbelohde type viscometer increased from 23 to 36 centipoises. The original solution was Newtonian in flow properties, but after the ageing with ferric chloride showed deviations from Newtonian flow. This indicated the presence of gel structures.

Discussion

It is evident from the experimental data that small amounts of impurities may cause rather large variations in the viscosity of polymer solutions. Only small changes in viscosity are observed when solutions of the polymers in pure solvents are aged in evacuated bombs (Tables I and II). Oxygen from the air and iron in the form of a salt are probably not the only materials that can cause instability. The effect does not appear to be specific since it occurs in a variety of polymer–solvent systems. The magnitude of the change in viscosity is not the same in all cases, which is to be expected, since different weight concentrations of the polymers were used in preparing the solutions.

Changes in the viscosity of a solution containing macromolecules could be caused by variations in (*a*) the degree of solvation of the polymer, (*b*) the orientation or configuration of the macromolecules in solution, (*c*) the chemical nature of the polymer, and (*d*) the molecular weight of the polymer. It is hardly conceivable that either of the first two mechanisms could cause irreversible gel formation. In none of the work was a regular trend in the saponification value observed, for example, Tables II and VII. Besides, polystyrene cannot be hydrolysed, yet its behaviour was similar to that of the other two polymers (Table VIII). It seems then that alterations in the molecular weight of the dissolved polymer cause the changes in the viscosity of the thickened solutions. Certainly this is indicated by the similar trends of the viscosity of the thickened solutions and of the intrinsic viscosity of the recovered polymer (Table V). These changes in molecular weight may be accompanied by variations in the structure of the polymer. This is suggested by the trend in the k' value for the series in Table V.

It is not possible to determine the rates of the degradation or of the gel-forming reactions from the change in viscosity with time, because the viscosity property depends upon such factors as the shape of the macromolecules, the degree of solvation, and the conditions of measurement. Owing to the shape of the viscosity–molecular-weight diagrams for such systems, small increases or decreases in molecular weight at higher concentrations may cause large changes in the viscosity.

Little may be said concerning the actual mechanism of the reaction between the polymer and dissolved iron salts or oxygen, nor can reactions between the solvents and these added substances be excluded entirely. For example, the degradation of the polymers in bis(2-chloroethyl) ether is greater than in the other solvents. This suggests the possibility of reaction of the impurities with bis(2-chloroethyl) ether, with the formation of compounds that also degrade the polymer. That the effects of iron salts and of oxygen may be interrelated is indicated by the fact that both ferrous and ferric chlorides cause gel formation in solutions of Gelva V-45 in bis(2-chloroethyl) sulphide in bombs, but not in bottles.

Oxygen appears to degrade the polymer chains while iron salts cause chain linking and frequently gel formation. The effect of iron seems to be chemical rather than catalytic, since a limiting concentration exists. In the case of bis(2-chloroethyl) ether and nitrobenzene this limit is between 0.01 and 0.001% as ferric chloride. The number average molecular weight of Gelva V-45 is approximately 140,000 (7), and, since approximately 10% by weight of the polymer was used in preparing the solutions, the ferric chloride and the polymer were present in nearly molar proportions. The gel-forming reaction is apparently quite irreversible, because several attempts to break the gels and recover the polymer were unsuccessful. Further speculation than this concerning the nature of the reaction between the iron salts and the polymer molecules appears unwarranted.

Acknowledgment

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THE MOLECULAR WEIGHT OF SOME POLYVINYL ACETATES[1]

BY R. McINTOSH[2] AND J. A. MORRISON[3]

Abstract

The number average molecular weights of two series of polymer samples, recovered from aged solutions of polyvinyl acetate in bis(2-chloroethyl) ether, have been measured using a dynamic type osmometer. It is shown that these number average molecular weights change from sample to sample in a manner similar to the intrinsic viscosities of the recovered polymers. This confirms previous results, which suggested that the change in viscosity of solutions of high polymers on ageing was due primarily to changes in the molecular weight of the dissolved polymer. A method of evaluating a relative non-uniformity coefficient for the polymers is suggested.

Introduction

In another paper (10), the effect of iron salts and of oxygen in causing changes in the viscosity of solutions of high polymers has been described. For solutions of polyvinyl acetate in bis(2-chloroethyl) ether, it was shown that the intrinsic viscosity of the recovered polymer changed in a manner similar to the viscosity of the aged solutions. This fact suggested that the molecular weight of the polymer was altered during the ageing process. However, since the viscosity property of solutions may also depend upon factors other than molecular weight of the solute, it was desirable to have an absolute measure of the molecular weight. Number average molecular weights of the polymers recovered from two series of aged solutions have now been measured using an osmometer, and are reported here. These results establish that molecular weight changes do occur during the ageing of polymer solutions.

The modified form of the Staudinger equation, $[\eta] = KM^a$, has been used to correlate the results. The slopes a from the plots of the logarithm of $[\eta]$ against the logarithm of M_n for the two series of polymers differ from the slope previously found for polyvinyl acetates (3, 11). A difference in a for polystyrene polymerized at different temperatures has been reported by Alfrey, Bartovics, and Mark (1). From the observation that the μ (4) and k' (5) factors for the polymers differed, these authors have been led to the view that the change in a is brought about by changed internal architecture of the polymer molecules. In the present instance, the variation in k' is very small and the slopes of the π/c versus c plots are the same within experimental error. It appears then that the change in a is due to some other factor, possibly changes in the heterogeneity of the polymer samples. In Part II an attempt is made to evaluate a relative non-uniformity coefficient, β. The development is based upon the fact that the average molecular weight deter-

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mined with an osmometer is a different average from that derived from the intrinsic viscosity.

Part I—Determination of Molecular Weights

Experimental

The osmometer was of the dynamic counter-pressure type. A full description of the cell and of the thermostat has been given (11), and no further comment is necessary here. The osmotic pressure measurements were made using dry acetone as solvent. The membranes were prepared by swelling No. 600 P.T. Cellophane (not waterproofed) in aqueous solutions of sodium hydroxide, followed by accommodation to the organic solvent. Two series of membranes were prepared, one series swollen in 1.5% sodium hydroxide, and the other in 4% sodium hydroxide. No difference in behaviour between the two types of membrane (except permeability to solvent) was observed. Both were completely impermeable to the polymer. Osmotic pressure values obtained with either type were concordant. Time lags in the establishment of equilibrium were short, and the slope of the π/c versus c plots was the same as that previously found for this type of membrane (11). No trend in osmotic pressure with time was observed. Refilling of the cell with solutions of the same concentration after an initial equilibrium value had been obtained was without effect.

The recovery of the polymers from aged solutions has been described (10). It is pertinent to emphasize again that changes in the chemical composition of the recovered polymers were within the limit of reproducibility of the analysis for acetate groups. Unfortunately, the quantitative comparison of the intrinsic viscosity and the number average molecular weight is subject to an uncertain error due to incomplete recovery of some of the polymer samples. Generally the yield on recovery was 98% or better, so that the error is probably not serious.

Results

The osmotic pressure data are given in Table I, and are represented graphically in Fig. 1. The π/c versus c plots for Samples 1 of both series were indistinguishable, and have been represented by a single line in Fig. 1. The polymer samples in Series I were recovered from solutions of polyvinyl acetate (Gelva V-45) in bis(2-chloroethyl) ether, aged in the presence of air at 60° C. The samples in Series II were recovered from solutions of Gelva V-45 in bis(2-chloroethyl) ether plus 0.003% ferric chloride, aged at 60° C. in glass bombs, which, after the solutions were degassed, were sealed at a pressure of 0.1 mm. of mercury. No peculiarities were observed in the determination of the osmotic pressures of Series I, but high values of osmotic pressure were observed near a concentration of 2.5 gm. per 100 cc. for the second sample of Series II, and at about 2.0 gm. per 100 cc. for the third sample. One additional sample of Series II was not investigated because of the narrowing concentration range over which it appeared feasible to work.

TABLE I

OSMOTIC PRESSURE DATA OF AGED POLYMERS

Series	Sample number	Membrane treatment	c*	π/c†	Limiting π/c at $c = 0$
I	1	1.5% NaOH	1.21	4.0_0	2.0_1
		1.5% NaOH	1.47	4.4_2	
		1.5% NaOH	1.58	4.7_7	
		1.5% NaOH	1.98	5.2_8	
		1.5% NaOH	2.36	5.9_8	
	2	4% NaOH	1.08	4.1_0	2.2_8
		4% NaOH	1.21	4.1_8	
		4% NaOH	1.46	4.7_5	
		4% NaOH	1.64	5.0_1	
	3	1.5% NaOH	1.00	4.1_0	2.4_3
		1.5% NaOH	1.56	5.0_5	
		1.5% NaOH	1.95	5.6_6	
	4	1.5% NaOH	0.97	4.4_6	2.7_5
		1.5% NaOH	0.99	4.2_8	
		1.5% NaOH	1.60	5.4_4	
		1.5% NaOH	1.78	5.7_0	
II	1	4% NaOH	1.17	3.8_5	2.0_1
		4% NaOH	1.57	4.5_7	
		4% NaOH	1.76	5.0_5	
		4% NaOH	2.04	5.4_5	
	2	1.5% NaOH	1.07	3.6_0	1.8_0
		4% NaOH	1.36	3.9_0	
		4% NaOH	1.19	3.8_0	
		4% NaOH	1.58	4.4_5	
		4% NaOH	1.82	4.6_8	
	3	1.5% NaOH	1.03	2.8_7	1.2_1
		1.5% NaOH	1.47	3.5_5	
		1.5% NaOH	1.95	4.3_5	
	4	1.5% NaOH	1.04	2.7_5	1.0_8
		1.5% NaOH	1.47	3.4_3	
		4% NaOH	1.77	3.8_8	

* *Concentration—grams of polymer/100 cc. of solution.*
† *π—osmotic pressure in centimetres of water.*

The derived data, $[\eta]$, k', M_n, and β are given in Table II. The values in Columns 3 to 6 have been reported (10), but are included again for convenience of comparison. The intrinsic viscosity of the first sample of Series II has been redetermined, the new value being 1.17 in place of 1.01 as given previously (10). The cause of the difference in intrinsic viscosity between Samples 1 of Series I and II is not clear. Qualitatively it has been observed that the addition of small amounts of ferric chloride brings about an immediate increase in the viscosity of polymer solutions.

The most important information in Table II is the changing value of M_n, which in both series follows a trend similar to that of the viscosity of the original solutions and of the intrinsic viscosity. It appears then that real changes in molecular weight occur when the polymer solutions are aged, and that these changes are the fundamental cause of the increase or decrease in viscosity. Certainly, the suggestion of Mead and Fuoss (9), that the changes in viscosity are due to alterations in the form of the polymer in solution, is not an adequate explanation for the results.

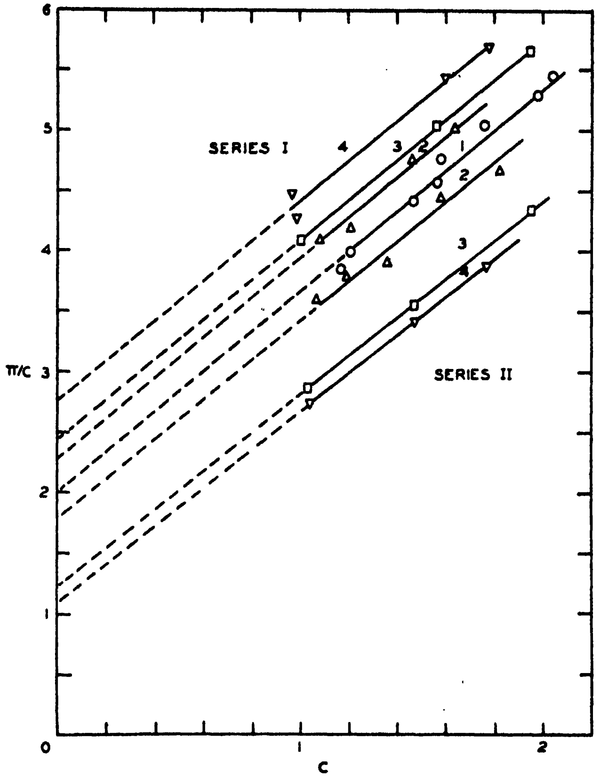

FIG. 1. *Plot of π/c versus c—data of Table I.*

TABLE II

VARIATION OF PROPERTIES OF SAMPLES WITH AGEING

Series	Original solution in bis(2-chloroethyl) ether						
	Sample number	Ageing time, days	Viscosity, poises	$[\eta]$	k'	M_n	β
I	1	0	3.70	1.07	0.34	128,000	2.1_4
	2	8	3.50	1.03	0.36	113,000	2.1_9
	3	87	3.25	0.98	0.36	105,000	2.1_8
	4	154	3.15	0.95	0.33	93,500	2.2_1
II	1	0	3.55	1.17	0.34	128,000	2.2_2
	2	1	5.45	1.24	0.37	143,000	2.2_1
	3	2½	8.70	1.59	0.38	220,000	2.1_9
	4	3	12.0	1.66	0.39	247,000	2.1_6

In Fig. 2 plots of log [η] against log M_n for Series I and II are shown. The best straight lines through the experimental points have slopes of 0.38 and 0.54 for Series I and II respectively, as compared with 0.63 for unaged polyvinyl acetates (3, 11).

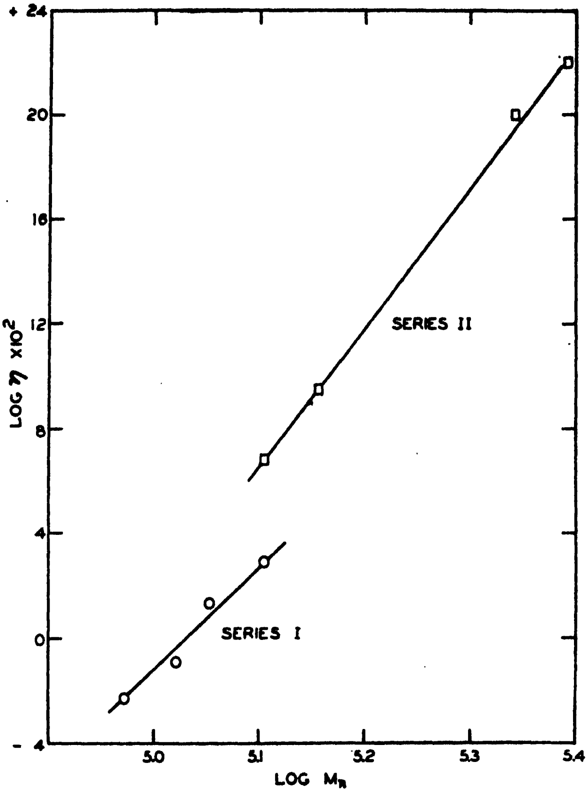

FIG. 2. *Plot of log* [η] *versus log* M_n*—data of Table II.*

Part II—Non-Uniformity Coefficient

Theoretical

The intrinsic viscosity of a heterogeneous sample of polymer in terms of the intrinsic viscosity of each species is given by

$$[\eta] = \frac{\Sigma\,[\eta]_i w_i}{\Sigma\, w_i} \tag{1}$$

where $[\eta]_i$ = intrinsic viscosity of the ith species

w_i = weight of the ith species.

As has been pointed out by Mark (8, p. 56) and Lansing and Kraemer (6), if the Staudinger rule is applicable,

$$[\eta]_i = K_{st} M_i \tag{2}$$

where M_i = molecular weight of the ith species

K_{st} = Staudinger constant,

the definition of intrinsic viscosity in Equation (1) states that the intrinsic viscosity is proportional to the weight average molecular weight. Recently the Staudinger rule has been replaced by the relation

$$[\eta]_i = KM_i^a \tag{3}$$

probably first suggested by Mark (7, p. 103) and verified since by Houwink (3) and Flory (2).

Substituting Equation (3) into Equation (1) yields

$$[\eta] = \frac{\Sigma KM_i^a w_i}{\Sigma w_i} = \frac{K\Sigma M_i^{1+a} n_i}{\Sigma M_i n_i} \tag{4}$$

where n_i = number of molecules of the ith species.

The number average molecular weight measured by the limiting osmotic pressure method is given by

$$M_n = \frac{\Sigma M_i n_i}{\Sigma n_i} \tag{5}$$

To evaluate the two averages a distribution function relating the number of molecules of given molecular weight to the molecular weight must be assumed. In so doing, the summations are replaced by integrations, but since the increments of molecular weight are small compared with the molecular weight, the error introduced is probably very small. It is desirable to choose a distribution function that has a single maximum and represents substantially zero numbers of molecules of very low molecular weight and of very high molecular weight. Theoretically there are probably several functions that could be used, but the one adopted here is the logarithmic distribution, which has been used by Lansing and Kraemer (6) in the form

$$\frac{dn}{N} = \frac{I}{\sqrt{\pi}} e^{-y^2} dy \tag{6}$$

where $y = \frac{1}{\beta} \ln \frac{M}{M_0}$

dn = number of molecules between y and $y + dy$

N = total number of molecules.

M_0 and β may be considered as parameters of the distribution function. M_0 is the value of M corresponding to the maximum value of the tangent to the distribution curve, while β is defined as the non-uniformity coefficient. For homogeneous materials β is zero, and for heterogeneous materials it has a positive value.

Introducing the distribution function Equation (6) into Equations (4) and (5),

$$[\eta] = \frac{\dfrac{2NK}{\sqrt{\pi}}\displaystyle\int_0^\infty M^{1+a}e^{-y^2}dy}{\dfrac{2N}{\sqrt{\pi}}\displaystyle\int_0^\infty Me^{-y^2}dy} \tag{7}$$

$$M_n = \frac{\dfrac{2N}{\sqrt{\pi}}\displaystyle\int_0^\infty Me^{-y^2}dy}{N} \tag{8}$$

whence,

$$[\eta] = K\,M_0^a e^{\beta^2\left[\left(\frac{1+a}{2}\right)^2-\frac{1}{4}\right]} \tag{9}$$

$$M_n = M_0\,e^{\frac{\beta^2}{4}} \tag{10}$$

Eliminating M_0 between Equations (9) and (10) gives

$$[\eta] = M_n{}^aKe^{\frac{\beta^2}{4}(1+a)a} \tag{11}$$

or

$$\ln\,[\eta] = a\,\ln M_n + \ln K + \frac{\beta^2}{4}(1+a)a \tag{12}$$

A plot of log $[\eta]$ against M_n will yield a straight line either if the polymers are homogeneous and β is zero, or if the polymers are heterogeneous and β is constant or else varies linearly with M_n. Relative changes of β, brought about by any reactions of the polymer where the molecular weight alone is altered, may be evaluated by the measurement of $[\eta]$ and M_n. The intercepts of the straight lines will depend upon β, and therefore the constant K cannot be determined with heterogeneous polymers. In the present instance, an arbitrary value must be chosen for K.

Results

In the calculation of β for the polymer samples in Series I and II, a was taken as 0.63 (11), and a value of 2.0×10^{-4} was selected arbitrarily for K. The values of β so determined are given in the last column of Table II. The change in β in either series is small, but qualitatively one would expect the trends that are observed. For Series I, if the degradation of each species is not complete, an extension of the molecular weight range in the sample would be expected. For Series II, a decrease in the degree of heterogeneity could be caused by a slightly greater rate of reaction of the lower molecular weight species.

However, the possible errors in the values of M_n may make meaningless the apparent changes in β. The errors in M_n are due principally to the long extrapolation of the π/c versus c plots that is necessary with the type of osmotic cell used. In addition, as has been pointed out, the quantitative comparison of the intrinsic viscosity and the number average molecular weight is subject to error due to incomplete recovery of the samples of polymer from the aged solutions.

Acknowledgment

The authors wish to express their thanks to Dr. O. Maass for his interest in this work and for arranging financial assistance.

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PREPARATION OF PICRYL CHLORIDE[1]

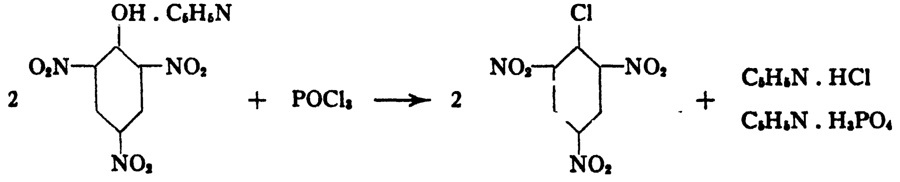
BY RAYMOND BOYER[2], E. Y. SPENCER[3], AND GEORGE F. WRIGHT[4]

Abstract

Picryl chloride can be prepared from pyridine picrate and either phosphorus oxychloride or phosgene in 97 to 100% yield. The pyridine used in this process is recoverable as its picrate and thus acts as a non-expended carrier during repeated preparations. Two of the chlorine atoms react in phosphorus oxychloride while only one in phosgene furnishes picryl chloride. The latter acid chloride is, however, more economical in use owing to its lower cost and molecular weight.

Picryl chloride can be prepared from one mole picric acid and two moles phosphorus pentachloride (1), but in our hands the yield was only 55% of the theoretical. The vigour of the reaction seemed to cause tar formation and to be potentially dangerous on the large scale. We modified Jackson and Gazzolo's procedure by addition of five moles of thionyl chloride and thus were able to carry out the reaction smoothly under reflux to give a 70% yield. The thionyl chloride evidently acted only as a solvent, since the use of a catalytic amount of phosphorus pentachloride in this solvent yielded no picryl chloride from picric acid. Sulphuryl chloride, phosphorus trichloride, and chlorosulphonic acid were likewise ineffective. None of these substances became reactive when catalytic amounts of benzoyl peroxide were added.

Phosphorus oxychloride also was unreactive toward picric acid alone, but we found that it reacted smoothly with pyridine picrate. Fifteen minutes' reflux in benzene solution gave a yield of good quality picryl chloride which was 98% of theoretical. Although two of the chlorine atoms in phosphorus oxychloride are available for picryl chloride formation the use of 1 : 2 ratio led to an impure product.



Practically, we have used about 0.7 moles of phosphorus oxychloride per mole of salt in order to obtain a 98% yield of good picryl chloride melting at 79° to 81° C.

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In the event that a considerable quantity of picryl chloride were needed, the process could be made both convenient and economical. The soluble pyridine salts, which remain in the aqueous liquors used to wash the benzene solution, may be precipitated by addition of picric acid to the warm aqueous liquors. This regenerated pyridine picrate (93% recovery) is entirely adequate for a subsequent preparation.

The reaction between picric acid and phosphorus pentachloride yields phosphorus oxychloride. Since both of these phosphorus halides are priced the same in quantity lots, it may be calculated stoichiometrically that a slight advantage in quantity manufacture would result by initial use of phosphorus pentachloride on picric acid, followed by recovery of the phosphorus oxychloride for subsequent utilization with pyridine picrate. This stepwise operation would be necessitated by the fact that phosphorus pentachloride (as well as phosphorus trichloride, sulphuryl chloride, and chlorosulphonic acid) will not react with pyridine picrate, although it will react with picric acid.

All such speculation respecting economical production of picryl chloride from the phosphorus halides was, however, cut short by the discovery that phosgene, which was unreactive toward picric acid at 100° C. during three hours' contact, reacted quantitatively with pyridine picrate. The salt was treated in an autoclave for two hours at 56° C. with 50% or greater excess of phosgene to give a 100% yield of crude picryl chloride melting at 79° to 80° C. This crude was the residue obtained by atmospheric evaporation of the recoverable phosgene followed by aqueous wash to remove the pyridine hydrochloride. Although only one of the chlorine atoms in phosgene is available for picryl chloride formation, the chloride affords a cost advantage of at least 20% over the process using phosphorus halides.

Most of our work was carried out in low pressure autoclave equipment, but it was found that 97% yield could be effected by condensing phosgene into pyridine picrate at 0° C. After one-half hour, the excess of phosgene was evaporated at room temperature and the residue washed with water to remove the recoverable pyridine hydrochloride.

The pyridine picrate used initially in this process was prepared in 98% yield by combination of the ingredients in ethanol. The salt, melting at 166° C., was much easier to filter than that prepared in aqueous solution from equivalent amounts of hot aqueous sodium picrate and pyridine hydrochloride. The melting point of this cheesy precipitate, 242° C., was unaffected by resolution and recrystallization from its own mother liquors or from ethanol, but when crystallized from pure water it melted at 166° C. When technical pyridine (average molecular weight of 107 in contrast to pyridine of 79) was used instead of pure pyridine for preparation of the salt, the precipitate melted at 88° to 153° C. as might be expected of a mixture of salts. This impure picric acid salt was, however, equally effective in picryl chloride preparation with that derived from pure pyridine.

The recovery of pyridine from the products prepared from phosphorus oxychloride was effected by precipitating calcium phosphate from the aqueous liquors used to wash the benzene solution of picryl chloride. After this treatment with an excess of lime, picric acid was added to the hot stirred filtrate until precipitation of pyridine picrate was complete. The lime treatment was, of course, not necessary when phosgene was used as the acid chloride. In either case the pyridine picrate was thoroughly air-dried before re-use.

Although the crude products from these preparations are not pure picryl chloride, which melts at 83° C., they are adequate for many uses. Thus this crude picryl chloride could be converted in 99% yield to N-methylpicramide, which in turn was pure enough that it could be converted in 97% yield to pure tetryl.

Experimental*

Preparation of Pyridine Picrate

Method 1.—To a solution of 22.9 gm. (0.1 mole) picric acid in 200 cc. of hot 95% ethanol was added 7.9 gm. (0.1 mole) of pyridine. A 98% yield (30.1 gm.) was filtered off the cooled solution. The salt melted at 166° C.

Method 2.—To a solution of 22.9 gm. (0.1 mole) of picric acid dissolved in 200 cc. of hot 2% aqueous sodium hydroxide was added 7.9 gm. (0.1 mole) of pyridine in 28.6 cc. of dilute hydrochloric acid. A cheesy precipitate, difficult to filter, was obtained on cooling. It weighed 28.1 gm. (91% of theoretical) and melted at 242° C. This melting point was unchanged after crystallization from ethanol or from the precipitating liquors but water recrystallization converted it to the ordinary pyridine picrate melting at 166° C.

Picryl Chloride from Phosphorus Oxychloride

One mole (308 gm.) of dry pyridine picrate was boiled for 15 min. under reflux with 0.67 mole (103 gm.) of phosphorus oxychloride in 250 cc. benzene. Both the precipitated oil and the benzene layer were washed several times with hot water. The benzene solution on evaporation yielded 73% of the theoretical amount of picryl chloride while the residue from the precipitated oil constituted 25% of the theoretical yield. The total (98% yield) picryl chloride melted at 79° to 81° C.

The aqueous washing liquors were treated with an excess of hydrated lime to remove phosphate. After filtration the solution was heated to 70° C. and stirred while one mole (229 gm.) of picric acid was added slowly to insure solution. The pyridine picrate that precipitated completely on cooling melted at 166° C. and weighed 298 gm. or 97% of theoretical. This was air-dried before re-use together with the evaporated benzene.

Picryl Chloride from Phosgene

Into one mole (308 gm.) of dry pyridine picrate in a light iron pressure vessel or bomb tube was poured or condensed 1.5 moles (148.5 gm.) of commercial phosgene. After two hours or less at 56° C. the pressure was released to distil off the excess phosgene. The remainder was blown with air to remove

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**All melting points are corrected.*

last traces of poisonous gas and was then ground in a mortar with three 500 cc. portions of water at 70° C. The remaining picryl chloride weighed 247 gm. (100% yield) and melted at 78° to 79.5° C.

The combined aqueous wash liquors were heated to 70° C. and stirred while 1 mole (229 gm.) of picric acid was added slowly. After cooling to complete precipitation the pyridine picrate was filtered off and air-dried to weigh 287 gm. or 93% of the amount originally added. Either quinoline or the mixture of pyridine, picolines, and lutidines known as "technical pyridine" works as satisfactorily except that filtration of the recovered pyridine salts is slightly more difficult.

This method of picryl chloride preparation may be varied by eliminating the heating period at 56° C. After the phosgene was poured or condensed into the pyridine picrate at 0° C., the mixture was let stand at this temperature for 30 min. and then warmed to 25° C. to remove the phosgene. The yield of picryl chloride, m.p. 78° to 79° C., from an otherwise identical procedure was 96.7% of theoretical. The yield was, however, decreased to 50% or less when gaseous phosgene was passed over thin layers of pyridine picrate either at 25° or 55° C. for 30 min.

Preparation of N-methylpicramide

The method of van Romburgh (2) was followed by adding 0.024 mole (0.74 gm.) of methylamine in 4 cc. methanol to 0.01 mole (2.47 gm.) of crude picryl chloride, m.p. 78° to 79.5°, in 3 cc. methanol at 20° C. The crystals were filtered off and washed once with methanol. The combined methanolic solutions were evaporated and the crystal crop recrystallized from benzene. In this manner a 99.2% yield (2.40 gm.) of N-methylpicramide, m.p. 110° to 110.5° C., was obtained.

Preparation of N-methyl-N-nitropicramide (Tetryl)

Treatment of 0.0025 mole (0.61 gm.) of N-methylpicramide, m.p. 110° to 110.5°, with 0.06 mole (4 cc.) of 70% nitric acid, followed by evaporation on the steam-bath gave a yellow residue. When this was water-washed and dried it represented a 97.0 yield of tetryl melting at 128° to 129° C.

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PREPARATION OF PICRAMIDE[1]

By E. Y. Spencer[2] and George F. Wright[3]

Abstract

The method of Kym for conversion of phenols into aromatic amines has been applied to picric acid. An 88% yield of picramide has been obtained by adjusting the reaction temperature to 173° C., the molar urea : picric acid ratio to 3 : 1, and the reaction time to 36 hr.

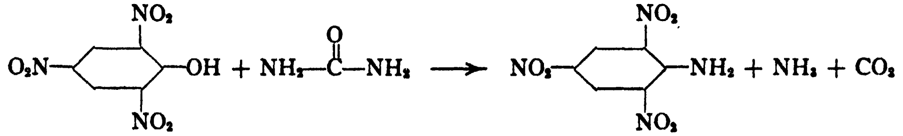
In connection with the preparation of tetranitrobenzene (2), we required a cheap, plentiful, and safe method for obtaining the necessary picramide. The method of Merz and Ris (4), which involves the action of 35% ammonia on nitrophenols to give aminonitrobenzenes, gave a charcoal-like product with picric acid after 16 hr. at 160° to 170° C. A control experiment involving picramide instead of picric acid under the same conditions showed that 88% of the picramide was recoverable and therefore would not have been destroyed under this reaction environment. Similarly no picramide could be obtained from picric acid and zinc chloride ammoniate ($ZnCl_2 . 2NH_3$) at 155° C., although a comparable experiment with picramide showed no degradation.

Kym (3) has reported that nitrophenols can be converted to aminonitrobenzenes by heating the phenol with urea. Thus he obtained a 75% yield of 2,4-dinitroaniline from one part of 2,4-dinitrophenol and three parts (9.2 moles) of urea at 208° C. for eight hours. We found that this method was applicable to the preparation of picramide.

Our first experiments were carried out for seven hours at 155° C. using Kym's 9.2 molar ratio of urea to picric acid. The 12% yield could be increased to 26% by increasing the reaction time to 16 hr. A further yield increase to 45% was effected by raising the temperature to 173° C. and this was augmented to 67% by reducing the molar urea–picric acid ratio to 4.5.

The reaction produces ammonia and ammonium carbonate as might be expected from Equation (I),

I



and on this basis an excess of urea would seem to be unnecessary. However, a water and acetone-insoluble by-product is formed which must arise by decomposition of the urea. This alternative consumption of urea may account for the fact that a low yield, chiefly ammonium picrate, was obtained when equimolar quantities of picric acid and urea were heated 16 hr. at 173° C. Two moles of urea per mole of picric acid was still not sufficient to supply reagent for both main and side-reactions, since a yield of 15% picramide was optimum under these conditions. The use of three moles of urea seemed, however, to supply an adequate excess.

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Contribution from Department of Chemistry, University of Toronto, Toronto, Ont.

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[3] *Professor of Chemistry.*

This 3 : 1 molar ratio of urea to picric acid produced 73% of picramide in 13 hr. Time of reaction, and not further excess of urea, was shown to be the limiting yield factor by evaporating to dryness the water-washing liquor from this latter picramide yield and then reheating aliquots of the residue for 24 hr. longer, with and without additional urea. A further 12% yield was obtained in either case. This finding was substantiated by a complete experiment wherein three moles of urea per mole of picric acid was heated 36 hr. at 173° C. to give an 88% yield of picramide melting at 187° to 188° C. A slightly higher (91%) yield of poorer product (m.p. 185° to 189° C.) was obtained at a reaction temperature of 183° C.

The fate of the reagents is shown in the following capitulation of this latter experiment.

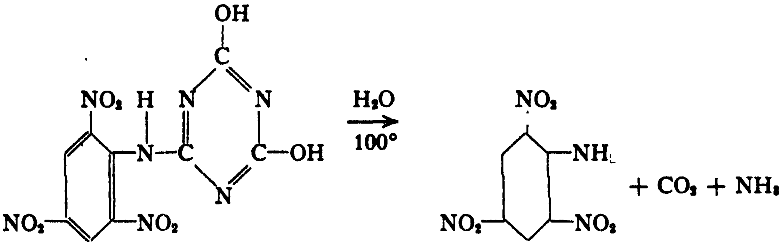
	Grams	Moles	Weight, gm.	Moles
Reagents:				
(Picric acid)	229	1		
(Urea)	180	3		
Products:				
Water soluble (urea)			31.8	0.53
Sublimate (ammonium carbonate by titration)			70.2	0.73
Gas evolved (ammonia by titration)			5.7	0.33
Picramide (m.p 185°–189°)			207.7	0.91
Acetone-insoluble (as derivatives of cyanic acid)			63.2	1.47(as cyanic acid)
(as "bound" picramide)			15.8	0.07
Total recovered			394.4	

This 96% material recovery affords some insight into the fate of the urea and the course of the reaction, although a thorough knowledge could be realized only by complete analysis of the acetone-insoluble material.

This analysis is not complete. Extraction with boiling water yields 25% of its weight as cyanuric acid. When the remainder is boiled with 600 parts of water, ammonia is produced, together with a small amount of cyanuric acid. The poorly crystalline material which precipitates on cooling represents 23% of the total; this material yielded 90% of its weight as pure picramide when it was extracted with acetone. Neither picric acid, melamine nor biuret could be detected.

This indicates that about 75% of the acetone-insoluble material is a condensation product of picrylurea. Although the solubility of the acetone-insoluble material in alkali would indicate that this might be picrylammelide,

II



the material must necessarily be more complex in order to account for the limited weight of picramide that is recovered after its decomposition. Further speculation seems fruitless until some means can be found to characterize further this intractable material. It must at present be considered a material bound by urea decomposition products from which, by boiling, sufficient picramide can be recovered to bring the total yield of the latter substance to 98% of the theoretical amount. It probably is significant that with increasing ratio of urea to picric acid the yield of acetone-soluble (free) picramide *decreased* while the amount of acetone-insoluble material increased.

The material balance (1 picramide: 1.79 NH_3 : 0.73 CO_2) shows, either that part of the carbon dioxide product according to Equation (I) is utilized in urea condensation, or, more probably, that the reaction follows an alternate course:

III $\quad ROH + NH_2CONH_2 \longrightarrow RNH_2 + HOOCNH_2$

IV $\quad HOOCNH_2 \longrightarrow H_2O + HCNO$

while the ammonia, ammonium carbonate, and the remainder of the cyanic acid involved in the acetone-insoluble material are derived by decomposition of urea. Such formulations are, of course, subject to urea decomposition equilibria at temperatures below 200° (5), nor is the intermediate formation of urea picrate and picrylurea excluded.

Experimental*

Picramide

One mole of picric acid melting at 120° to 121° C (229 gm.) was mixed with three moles (180 gm.) of technical urea in a 1 litre distilling flask equipped with a side-arm of 20 mm. diameter. The effluent from the receiver was passed through standard acid. At the end of the experiment both the ammonium carbonate in the receiver and the ammonia absorbed in the acid were estimated independently. The reaction flask neck was equipped with a thermometer with bulb immersed in the reagents.

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* *Melting points corrected against known standards.*

The reaction flask was suspended with its equator 4 to 5 inches below the lip of a 3 litre beaker. Above the equator was coiled copper tubing to act as a condenser, and the flask neck was surrounded with a loosely fitting lid to eliminate bath losses owing to draughts. The beaker was filled about 1 inch in depth with *o*-dichlorobenzene (b.p. 183° C.) or a mixture of this with *p*-dichlorobenzene in case a lower temperature such as 173° C. was desired. A bare nichrome heating coil (250 watt) was immersed in the dichlorobenzene.

After 36 hr. reflux the flask content was removed from the flask with 1500 cc. water at 40° C. The aqueous washings were concentrated and the amount of recovered pure urea (m.p. 130° to 165° C.) was determined in this concentrate by dry weight. The water-insoluble portion of the reaction mixture was eluted with 2,000 cc. acetone in a Soxhlet extractor. The picramide was recovered from this acetone solution by evaporation of the solvent to weigh 207.7 gm. (91% of theoretical) and melt at 185° to 189° C. Further purification from acetone raised this melting point to 188° to 189° C. with a recovery of 88%.

The brown acetone-insoluble product dissolved, for the most part, slowly in 20 to 30% alkali to yield, after 20 hr., the insoluble crystalline trisodium cyanurate. Alternatively 25% of the acetone-insoluble material could be recovered as cyanuric acid by five-minute extraction with 25 parts of boiling water. This compound was identified by its crystal form, its loss of solvate water on heating to 56° (15 mm.) and by the titrimetric conversion of its trisodium salt to the disodium salt using phenolphthalein as indicator (1).

A 2.18 gm. aliquot of the cyanuric acid-free acetone-insoluble material was boiled one hour with 600 parts of water and filtered hot. The precipitate that appeared on cooling was filtered off, dried, and 0.5 gm. was boiled for 30 min. with 25 ml. acetone. The filtered solution was evaporated under 15 mm. to yield 0.43 gm. of picramide, m.p. 188° to 189° C. This melting point was not depressed by admixture of the product with an authentic sample.

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CHLORINATION BY AQUEOUS SODIUM HYPOCHLORITE[1]

By C. Y. Hopkins[2] and Mary J. Chisholm[2]

Abstract

New instances of nuclear chlorination of benzene derivatives by the action of cold aqueous sodium hypochlorite are reported. The reaction gives good yields of monochloro derivatives when the orientation is favourable.

Introduction

It is known that certain cyclic compounds can be halogenated by the action of aqueous hypohalites. Chlorination of benzoic acid by aqueous sodium hypochlorite was studied by Smith (12). He obtained a mixture of the three isomeric monochlorobenzoic acids as well as some dichloro acid. Salicylic acid undergoes chlorination in the same way, yielding a mixture from which some monochloro-salicylic acid can be isolated (4).

Nuclear chlorinated products have been prepared in the present work from various substituted benzoic acids, arylacetic acids, aryloxyacetic acids, and arylaldehydes, using sodium hypochlorite as the reagent. The results indicate that this method of halogenation is more widely applicable than previously supposed.

The procedure is extremely simple. The substance is dissolved or suspended in dilute alkali and mixed with sodium hypochlorite solution. It is left for an hour at ordinary temperature with occasional stirring. The product is then removed.

Certain substances, in which the orientation is most favourable, give monochloro derivatives in almost theoretical yield. These include vanillin, anisic acid, and piperonylacetic acid. The position taken up by halogen is the same as in ordinary non-aqueous chlorination. There is apparently no oxidation of the aldehyde group in the reaction with vanillin.

Experimental

A solution containing one mole of sodium hypochlorite per litre was prepared as the reagent (6). A suspension of calcium hypochlorite may be used but gives slightly lower yields. The general method of chlorination is illustrated by the reaction of sodium hypochlorite solution with anisic acid as follows:

Anisic acid (3.8 gm., 1/40 mole) was dissolved in 150 cc. of water and 25 cc. of 4% sodium hydroxide solution. It was cooled to 20° C., and mixed with 50 cc. (1/20 mole) of sodium hypochlorite solution. The temperature was

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[2] *Chemist.*

maintained at 20° C. for one hour with occasional stirring. Upon acidifying, a precipitate of almost pure 3-chloroanisic acid was obtained. The yield was 3.9 gm. (80% of theory). After one crystallization from toluene it melted at 215° C.

The experiments are summarized in Table I.

TABLE I

CHLORINATION PRODUCTS

Starting material	Moles NaOCl	Substitution product	Yield, %	M.p. after recrystallizing, °C.*	Reference
Anisic acid	2	3-chloro-	80	215	(2)
Vanillic acid	2	5-chloro-	85	242 to 244	(10)
p-Hydroxybenzoic acid	2	3,5-dichloro-	50	256 to 258	(5)
m-Methoxybenzoic acid	2	6-chloro-	60	170 to 171	(7)
2-Hydroxy-4-acetoxy-benzoic acid	2	5-chloro-	40	176 to 177	
Piperonylacetic acid	2	6-chloro-	80	177 to 178	(8)
Anisylacetic acid	1	3-chloro-	50	94 to 95	(8)
Vanillin	1.5	5-chloro-	90	164 to 165	(9)
Piperonal	1 or 2	6-chloro-	Poor	106 to 110	(13)
2,4-Dihydroxy-benzaldehyde	1.3	5-chloro-	80	156 to 157	(1, 3)
Phenoxyacetic acid	4	2,4-dichloro-	75	138 to 139	
2-Chlorophenoxy-acetic acid	2	2,4-dichloro-	80	138 to 139	
2-Methylphenoxy-acetic acid	1	4-chloro-	85	118 to 119	

* *Melting points are not corrected.*

Notes on the Products

5-Chlorovanillic acid.—This product was also made by chlorinating vanillic acid in chloroform by gaseous chlorine. It is considered to be 5-chlorovanillic acid since bromination by the same procedure is known to give 5-bromovanillic acid. The melting point agrees with that given by Raiford and Potter (10) for 5-chlorovanillic acid prepared from 5-chlorovanillin. The substance is readily soluble in ethanol and ether, slightly soluble in toluene, and insoluble in chloroform and hexane.

Chlorination of p-hydroxybenzoic acid.—A monochloro derivative could not readily be isolated.

2-Hydroxy-4-acetoxy-5-chlorobenzoic acid.—β-Resorcylic acid itself did not react normally with sodium hypochlorite, but monoacetyl-β-resorcylic acid gave the monochloro derivative without difficulty, m.p. 176° to 177° C. This substance has not been reported hitherto. Upon hydrolysis, it yielded 2,4-dihydroxy-5-chlorobenzoic acid, m.p. 218° C. (11).

6-Chloropiperonylacetic acid.—Found: Cl, 16.34, 16.61%. Calc. for $C_9H_7O_4Cl$: Cl, 16.55%. It did not depress the melting point of an authentic sample prepared by the method of Naik and Wheeler (8). The substance is readily soluble in alcohol, ether, and acetic acid, and is moderately soluble in benzene and chloroform. It is insoluble in hexane.

5-Chlorovanillin.—This substance was identified by mixed melting point with an authentic sample prepared by the method of Raiford and Lichty (9). It crystallizes from water in small plates. It is soluble in alcohol, moderately soluble in benzene, and sparingly soluble in water.

6-Chloropiperonal.—Piperonal gave a mixture of chlorinated products from which 6-chloropiperonal was isolated in poor yield, m.p. 106° to 110° C.

5-Chloro-2,4-dihydroxybenzaldehyde.—This product is evidently the monochloro derivative prepared by Gattermann (3), m.p. 157° C. The position of the chlorine group was established by Chakravarti and Ghosh (1).

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THE FATTY ACIDS OF HARE'S-EAR MUSTARD SEED OIL[1]

By C. Y. Hopkins[2]

Abstract

The fatty oil of hare's-ear mustard seed (*Conringia orientalis* L.) was examined. Constants of the oil were determined and a partial separation of the fatty acids was carried out by the methyl ester fractionation method. Palmitic, oleic, linoleic, eicosenoic, erucic, and lignoceric acids were identified. Erucic acid was found to be present in largest amount. The oil resembles rapeseed and other Cruciferae seed oils in this respect. The content of eicosenoic acid is estimated to be not more than 12% of the total fatty acids.

Introduction

The screenings from grain grown in Western Canada contain quantities of weed seeds of the Cruciferae. During a study of the economic utilization of screenings, the fatty oils of a number of these seeds were examined and it was found that the oil of hare's-ear mustard seed (*Conringia orientalis* L. (Dumort.))* closely resembles rapeseed oil in its physical characteristics. The examination of the fatty acids of hare's-ear mustard seed oil was then undertaken.

Experimental

The seed was obtained from a commercial sample of grain screenings. It was separated from the mixture of weed seeds therein by means of a machine specially constructed for the purpose in the laboratory. Small amounts of chaff and hulls were removed by aspiration. Three kilos of the seed was ground in a small roller mill and extracted with petroleum ether in an apparatus of the Soxhlet type. The yield of oil was 29.5% of the air-dry material. It was bright yellow in colour and had the characteristics shown in Table I.

TABLE I

Characteristics of the oil

Property	Hare's-ear mustard seed oil	Rapeseed oil (8)
Iodine number	107	98–106
Saponification number	173	170–178
Sp. gr. 15° C.	0.9135	0.914–0.916
Refractive index, 25° C.	1.4714	1.471

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* *The plant is also known under the following names: Brassica orientalis, Brassica perfoliata, Erysimum orientale, Erysimum perfoliata, Conringia perfoliata.*

The quantitative examination of the fatty acids was carried out according to the general method of Hilditch and co-workers (6). The oil was saponified by means of alcoholic potash, and the resulting anhydrous soap was mixed with pure sand and extracted thoroughly with acetone to remove the non-saponifiable portion. The residual soap was converted into the corresponding mixed fatty acids and these in turn were treated with lead acetate in boiling alcohol to form the lead salts. The latter were separated into three groups as described by Hilditch, Riley, and Vidyarthi (7), viz., those insoluble both in alcohol and in ether (*S*), those insoluble in alcohol but soluble in ether (*E*), and those soluble in alcohol (*A*).

The three groups of lead salts were converted separately to fatty acids. Each group of acids was esterified with methyl alcohol.

The esters were fractionally distilled *in vacuo* using a heated column with metallic packing, an oil-pump maintaining a vacuum of 2.5 mm. or less and a receiving device permitting uninterrupted distillation.

Examination of S Esters

The result of the fractionation of the *S* esters is shown in Table II.

TABLE II

FRACTIONATION OF *S* ESTERS

Fraction	Distillation range, °C., reduced pressure	Weight, gm.	Iodine value	Refractive index, 25° C.
*S*1	-123	2.5	14.2	1.4292
*S*2	123–150	11.0	17.1	1.4416
*S*3	150–181	7.8	63.6	1.4503
*S*4	181–200	26.6	70.9	1.4550
*S*5	200–205	20.0	70.4	1.4548
*S*6	Residue	54.8	63.7	—
		122.7		

Fraction *S*1 appeared to consist chiefly of non-acidic matter. Neither palmitic nor oleic acid could be detected.

Fraction *S*2 was saponified and the acids were recrystallized from alcohol. They yielded palmitic acid in quantity, m.p. 61° to 62° C.* (alone and mixed with an authentic specimen), neutralization equivalent, 257 (palmitic acid, 256). The acids from the mother liquor were treated with alkaline permanganate solution by the method of Lapworth and Mottram (9) in order to hydroxylate the unsaturated acids. After removal of palmitic acid by solution in hexane, the dihydroxy acids were recrystallized from ethyl acetate, and proved to consist chiefly of a dihydroxystearic acid, m.p. 116° to 117° C. It is more soluble in ethyl acetate and in ether than is the ordinary 9, 10-dihydroxystearic acid and is evidently produced from the same oleic acid found by Hilditch and others in rapeseed oil (7). The dihydroxystearic acid reported by Hilditch melted at 117° to 118°C. Its constitution was not established definitely.

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* *Melting points are not corrected.*

In addition, a very small amount of a second dihydroxy acid melting indefinitely at 125° C. was obtained, and this is presumably the dihydroxystearic acid (m.p. 132° C.) from ordinary 9 : 10 oleic acid. Linoleic acid was absent.

The acids from *S*3 were mainly unsaturated. After the usual oxidation, a small proportion of saturated acid melting at 54° to 56° C. was obtained. The hydroxylated acids were extracted with dry ether in a Soxhlet. The extract yielded the dihydroxystearic acid, m.p. 115° to 116° C., in quantity, and the residue had a melting point of 121° to 122° C., indicating the presence of the ordinary 9 : 10 oleic acid.

Fraction *S*4 was hydroxylated in the usual way and yielded a hydroxy acid that melted at 128° to 129° C. when recrystallized from ethyl acetate. This acid produced a depression in melting point when mixed with either 9, 10-dihydroxystearic acid or dihydroxybehenic acid. Its identification as dihydroxyeicosanoic acid is described in a subsequent paragraph. Lesser quantities of another unsaturated acid and of a saturated acid were indicated. Linoleic acid was absent.

The acids from *S*5 contained erucic acid, which gave dihydroxybehenic acid, m.p. 130° to 130.5° C. (alone and mixed with an authentic sample), and a saturated acid, m.p. 82° to 84° C., considered to be lignoceric acid.

The residue (*S*6) was assumed, from the analytical figures and analysis of the previous fraction, to contain only erucic and lignoceric acids.

Examination of E Esters

The *E* esters were fractionated in the manner described previously and the analysis of the various fractions was carried out in the same way as for the *S* esters.

The result of the fractionation is shown in Table III.

TABLE III

FRACTIONATION OF *E* ESTERS

Fraction	Distillation range, °C., reduced pressure	Weight, gm.	Iodine value	Refractive index, 25° C.
*E*1	90–127	1.6	42.7	1.4338
*E*2	127–168	5.9	52.4	1.4471
*E*3	168–171	33.5	111.5	1.4549
*E*4	171–174	19.9	118.8	1.4561
*E*5	174–176	16.5	103.9	1.4574
*E*6	176–184	12.6	92.7	1.4588
*E*7	184–188	43.5	82.6	1.4545
*E*8	188–193	14.6	77.9	1.4552
*E*9	193–198	43.7	73.3	1.4555
*E*10	Residue	51.1	70.8	—
		242.9		

Fraction *E*2, after saponifying and hydroxylating, yielded palmitic acid, m.p. 61° to 62° C. when recrystallized from alcohol. The hexane-insoluble hydroxy acids gave tetrahydroxystearic acid (from linoleic acid), m.p. 173° C., after recrystallizing from alcohol. There was also obtained a dihydroxy acid melting at 117° to 118° C., evidently from the same oleic acid described under *S*2.

Fraction *E*3 yielded the ordinary 9,10-dihydroxystearic acid, m.p. 128° to 130° C., alone and mixed with an authentic sample.

The acids from *E*5 were found to contain linoleic acid, identified as the tetrahydroxy derivative. Other hydroxy acids, not readily separable were obtained. There was little or no saturated acid.

The acids from *E*7, a large fraction in the C_{20} range, were examined in detail. A small proportion of linoleic acid was found. There was obtained a considerable quantity of dihydroxyeicosanoic acid, m.p. 129° to 130° C., as in *S*4.

There was also found, after hydroxylation, a hexane-soluble acid, or mixture of acids, which was unsaturated and melted at 46° to 48° C. This substance is described in a subsequent paragraph.

Fraction *E*8 contained no linoleic acid but was otherwise similar in composition to *E*7. Fraction *E*9 was found to be almost pure methyl erucate. Erucic acid, m.p. 32° to 34° C., was isolated and dihydroxybehenic acid was also prepared.

Examination of A Esters

The result of the fractionation of the *A* esters, the most unsaturated group, is shown in Table IV.

TABLE IV

FRACTIONATION OF *A* ESTERS

Fraction	Distillation range, °C., reduced pressure	Weight, gm.	Iodine value	Refractive index, 25° C.
*A*1	90–160	2.7	56.7	1.4507
*A*2	160–165	4.6	104.0	1.4571
*A*3	165–172	41.3	135.7	1.4572
*A*4	172–176	18.5	133.5	1.4590
*A*5	176–187	17.2	100.8	1.4572
*A*6	187–194	15.5	86.0	1.4558
*A*7	194–210	20.9	78.2	1.4560
*A*8	Residue	24.0	76.5	—
		144.7		

The acids from *A*2 yielded palmitic acid, m.p. 61° to 62°C. There was only a trace of saturated acid in *A*3. Fraction *A*4 contained much linoleic acid, obtained as tetrahydroxystearic acid, m.p. 172° C. Oleic acid is presumed to be present but it was difficult to purify the corresponding dihydroxy derivative.

Fraction *A*7 gave dihydroxybehenic acid (from erucic acid), m.p. 126° to 127° C. There was some indication of the presence of a doubly unsaturated acid, evidenced by the formation of a hydroxv derivative relatively insoluble in ethyl acetate.

A complete list of the acids that were identified is given in Table V.

TABLE V

IDENTIFICATION OF CONSTITUENT ACIDS

Chain length	Acid	Where found	Identified as	M.p. found, ° C.
C_{16}	Palmitic	*S*2, *E*2, *A*2	Palmitic acid	61– 62
C_{18}	Oleic	*S*2, *S*3, *E*2	Dihydroxystearic acid	116–117
				117–118
		*E*3	9,10-Dihydroxystearic acid	128–130
	Linoleic	*E*2, *E*5, *E*7, *A*4	Tetrahydroxystearic acid	173
C_{20}	Eicosenoic	*S*4, *E*7, *E*8	Dihydroxyeicosanoic acid	128–129
				129–130
C_{22}	Erucic	*S*5, *E*9, *A*7	Erucic acid	32– 34
			Dihydroxybehenic acid	130
C_{24}	Lignoceric	*S*5	Lignoceric acid	82– 84

The hexabromide test was applied to the original mixed fatty acids. The test showed that little or no linolenic acid is present. It was judged that the amount could not be more than 1% of the total fatty acids.

Dihydroxyeicosanoic Acid

Treatment of certain fractions of the fatty acids with cold alkaline permanganate solution resulted in the isolation by crystallization from ethyl acetate of a substance identified as dihydroxyeicosanoic acid.

The procedure was as follows: 5 gm. of a distilled fraction of the methyl esters was saponified and the solution was evaporated to a paste. The latter was dissolved in 3 litres of water, made neutral, and 5 gm. of sodium hydroxide added. The solution was kept at 15° C. while 400 cc. of 1% potassium permanganate solution was added with stirring. The mixture was stirred for 15 min. and was then decolorized by passing in sulphur dioxide. It was acidified by the addition of concentrated hydrochloric acid.

The white, flocculent precipitate was dried and extracted in a Soxhlet with hexane to remove saturated acids, then with dry ether to remove most of the dihydroxystearic acids. The remainder was recrystallized from ethyl acetate. In the case of the acids from *E*7, which gave the largest quantity of the product, the crystals melted at 129° to 130° C. The same substance was obtained from *E*8 (m.p. 129° to 130° C.) and *S*4 (m.p. 128° to 129° C.).

It behaved as a single substance when subjected to repeated fractional crystallization. In admixture with known substances, it melted as follows:

with 9,10-dihydroxystearic acid of m.p. 132° C., 120° to 123° C.

with 13,14-dihydroxybehenic acid of m.p. 130° C. 123° to 126° C.

with 11,12-dihydroxyeicosanoic acid† of m.p. 130.5° C., 130° to 130.5° C.

Found: C, 70.2, 70.1; H, 11.8, 11.8%; equiv., 347; iodine number, 0.
Calc. for $C_{20}H_{40}O_4$: C, 69.7; H, 11.7%; equiv., 344.5; iodine number, 0.

A portion of the same methyl ester fraction was oxidized by hydrogen peroxide by the method of Hilditch (4). The resulting dihydroxyeicosanoic acid melted at 94° to 95.5° C. It has not been described previously.

In admixture with the corresponding dihydroxy acids prepared from oleic and erucic acids, it melted as follows:

with 9,10-dihydroxystearic acid of m.p. 94° to 95° C., 87° to 89° C.

with 13,14-dihydroxybehenic acid of m.p. 98° to 99° C., 88° to 93° C.

The dihydroxy acid of m.p. 129° to 130° C. was subjected to oxidation by periodate according to the method of Baldwin and Parks (1). The products gave an alkali-soluble semicarbazone, m.p. 156° to 157° C., which depressed the melting point (by more than 10°) of the corresponding semicarbazones prepared in the same way from ordinary oleic and erucic acids. The mixed melting points were as follows:

with azelaic semi-aldehyde semicarbazone of m.p. 162° to 163° C., 140° to 145° C.

with brassylic semi-aldehyde semicarbazone of m.p. 160° to 161° C., 142° to 144° C.

Found: N, 16.2, 16.3%. Calc. for undecanoic semi-aldehyde semicarbazone ($C_{12}H_{23}O_3N_3$) : N, 16.33%.

An alkali-insoluble semicarbazone, m.p. 93° to 94° C., was also isolated. It gave no depression of melting point when mixed with nonaldehyde semicarbazone.

It is concluded from these results that the original acid has nine carbon atoms to the left of the double bond and that the portion of the chain to the right of the double bond has 11 carbon atoms. The original substance is therefore considered to be 11 : 12 eicosenoic acid.

Additional Evidence of the Presence of Eicosenoic Acid

The first indication of the presence of a C_{20} acid was the unexpectedly large fraction (*E*7) of methyl esters distilling midway between the boiling points of the C_{18} and C_{22} esters (see Table III).

There was a similar but smaller intermediate fraction (*S*4) obtained from the *S* esters. The *A* esters did not yield a readily recognizable C_{20} fraction.

The *E* esters therefore appear to contain the largest proportion of C_{20} acid or acids. Eicosenoic acid, if present, would be expected chiefly in the *E* esters, which are prepared from the lead salts of intermediate solubility, i.e., less soluble than lead linoleate but more soluble than lead palmitate. The separation by lead salts is, of course, far from complete.

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† *Kindly furnished by Professor Hilditch.*

Fraction *E7*, believed to consist largely of C_{20} acids, had equivalent weight 321 and iodine number 82.6. The corresponding figures for methyl eicosenoate are: equivalent weight, 324; iodine number, 78.2.

The second and positive indication of the presence of eicosenoic acid was obtained by the preparation of dihydroxyeicosanoic acid and comparison with a genuine sample, as described above.

The third indication of a C_{20} acid was the isolation during the permanganate oxidation of a solid, unsaturated acid melting in the neighbourhood of 50° C. This substance was obtained in rather small amounts from the treatment of fractions *E7*, *E8*, *S4*, and *A7*. It was isolated by extracting the resulting mixture of acids with hexane, in which it is soluble. Any saturated acid would, of course, be present with and contaminate it. It was at first thought that it might be the elaidic form of erucic acid, but, on treating genuine erucic acid with alkaline permanganate in the usual way, no such product was found.

The substance can be recrystallized from alcohol. The sample from *E7* had the following properties: m.p. 47° to 49°C., iodine number, 73; equivalent weight, 319. Eicosenoic acid requires: iodine number, 82; equivalent weight, 310. The low iodine number suggests the presence of saturated acids. An attempt to isolate this acid directly from the *E7* esters via the lead salt was unsuccessful, the resulting acid having a melting point no higher than 10° to 15° C.

Proportions of Fatty Acids

Calculation of the exact proportions of the various fatty acids requires more data than are available here. Furthermore, the presence of eicosenoic acid, in addition to the common acids, makes the calculation much more difficult. A rough estimate can be made by reference to the distillation data, the quantities of acids isolated from the various fractions, and the iodine numbers of the fractions.

The proportions of certain acids are estimated on this basis as follows (Table VI):

TABLE VI

ESTIMATED PROPORTIONS OF CERTAIN ACIDS (AS METHYL ESTERS)

Acid	*S* acids, gm.	*E* acids, gm.	*A* acids, gm.	Total wt., gm.	Total %
Palmitic	9	2	1	12	2
Other saturated acids	11	0	0	11	2
Linoleic	0	27	45	72	15

The remaining acids are oleic, eicosenoic, and erucic. These three comprise about 80% of the total acids. An estimate of the proportion of each can be made very roughly from the weight of the various fractions obtained in the distillations (Table VII).

TABLE VII

ESTIMATED PROPORTIONS OF ETHYLENIC ACIDS (AS METHYL ESTERS)

Acid	*S* acids, gm.	*E* acids, gm.	*A* acids, gm.	Total wt., gm.	Total %
Oleic	19	91	37	147	29
Eicosenoic	12	31	17	60	12
Erucic	68	89	42	199	40

Calculation of the iodine number from these figures gives a result lower than that for the original oil. Undoubtedly some of the more unsaturated components have been lost by oxidation and polymerization during the process of separation. It may be assumed that the content of linoleic acid is higher than 15%.

The composition of the fatty acids can therefore be given approximately as follows:

Palmitic	2%
Other saturated acids	2
Oleic	20-30
Linoleic	15-20
Erucic	35-45
Eicosenoic	Remainder

The percentage of eicosenoic acid as shown in Table VII is a broad estimate. The author is of the opinion that the amount may be somewhat less than 12% of the total fatty acids.

Discussion

The oil under examination is seen to resemble other Cruciferae oils in having erucic acid as its principal component. The only marked difference from the oils of rape, ravison, and mustard seed is the presence of eicosenoic acid. The author has not found any previous report of positive identification of this acid in vegetable oils. However, it has been isolated from a vegetable wax from the seeds of *Simmondsia californica* (10).

Eicosenoic acid is found in fish and marine animal oils, especially in cod liver oil (3), dogfish liver oil, and sperm oil. There is little information concerning the properties of the isomeric eicosenoic acids on record, and this fact adds to the difficulty of detection and positive identification.

Cis and *trans* 11 : 12 eicosenoic acids were prepared synthetically by Vesely and Chudozilov, who report that the *cis*-form is probably identical with gadoleic acid from cod liver oil, m.p. 23° to 24° C. (12). On the other hand, Toyama has shown by ozonolysis that the cod liver oil acid is 9 : 10 eicosenoic acid (11). Bodenstein prepared 11 : 12 eicosenoic acid by degrading erucic acid and gave the melting point as 50° C. (2). This may be the *trans*-form which Vesely found to melt at 53° to 54° C. The acid from *Simmondsia* seeds was identified as 11 : 12 eicosenoic acid but its melting point was not stated.

There is no apparent reason for the rarity of eicosenoic acid in the vegetable kingdom. It may occur in small quantity in a number of vegetable oils and have been overlooked by investigators. Examination of the data of Hilditch and co-workers for rapeseed and other Cruciferae oils indicates, however, that if eicosenoic acid is present it must be in comparatively small amount.

It is difficult to account for the fact that rapeseed and ordinary mustard seed oils contain large proportions of oleic (C_{18}) and erucic (C_{22}) acids but apparently no eicosenoic acid (C_{20}). In other fats that have been analysed in detail, all the even-numbered acids are present and form a series without gaps. Two of these are shown in Table VIII.

TABLE VIII

OCCURRENCE OF FATTY ACIDS IN SERIES

Saturated acids in coconut oil (5)		Unsaturated acids in sperm whale blubber (5)		Unsaturated acids in rapeseed oil (5)	
C_8	7.9%	C_{14}	4%	C_{14}	—
C_{10}	7.2	C_{16}	27	C_{16}	—
C_{12}	48.0	C_{18}	37	C_{18}	48%
C_{14}	17.5	C_{20}	19	C_{20}	—
C_{16}	9.0	C_{22}	1	C_{22}	50
C_{18}	2.1				

In the majority of seed fats, C_{16} and C_{18} acids make up almost the whole fatty acid content. The mechanism of elaboration in these seeds must therefore favour the C_{16} and C_{18} chain lengths. Cruciferae seeds have a tendency to secrete C_{22} acid in addition to C_{18} acids. The factor or factors leading to the production of unsaturated C_{20} acids in plants must occur but rarely, although the saturated acid, eicosanoic, is fairly common. In the species described in this paper, there is evidently a tendency to produce minor amounts of eicosenoic acid as well as the C_{18} and C_{22} acids. It may be noted that *Conringia orientalis* differs botanically in many respects from the *Brassica* species. The latter include rape and common mustard, in whose seeds eicosenoic acid has not been found.

Acknowledgment

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VAPOUR PHASE OXIDATION OF ETHYL LACTATE[1]

BY MARSHALL KULKA[2]

Abstract

A method has been developed for the vapour phase oxidation of ethyl lactate to ethyl pyruvate (yield, 68%), using air as oxidant and a platinum catalyst prepared by electrolytic deposition.

The oxidation of ethyl lactate in the liquid phase generally results in a low yield of ethyl pyruvate since the latter is susceptible to degradation and further oxidation. Hurd and Filachione (2) were able to prepare ethyl pyruvate in 42% yield by first condensing ethyl lactate with triphenylmethyl chloride and then pyrolyzing the condensate at 300° C. A patent (1) describing a process for the manufacture of esters of oxy-acids claims that ethyl lactate can be oxidized successfully (60% yield) by passing it mixed with air through a pipe 10 metres long, charged with vanadium pentoxide that had been precipitated on pumice stone, and heated at 250° to 255° C.

Mixtures of ethyl lactate and ethyl pyruvate are difficult to separate by fractional distillation because of the proximity of their boiling points (151° to 153° C. and 146° to 148° C. respectively). In this investigation it was decided to search for a catalyst that would direct the oxidation to complete conversion and thus avoid the difficult separation of the oxidation product and starting material. The catalysts that proved unsatisfactory were, copper or brass gauze, copper sulphate reduced with chromous chloride (4), ferrous vanadate (3), copper vanadate (3), vanadium pentoxide on asbestos, and silver on copper gauze with which at temperatures of 250° to 300° C. only a 35 to 50% conversion could be obtained. Platinum gauze coated electrolytically with a layer of platinum black was found to be the most desirable catalyst for this reaction. In the presence of this catalyst oxidation proceeded at a lower temperature and with almost complete conversion (yield, 68%). However, care had to be exercised in the preparation of the platinum surfaces, since platinizing under slightly different conditions produced catalysts varying in degree of activity. The oxidation reaction was extremely exothermic so that the oxidant (air) had to be diluted with inert gases such as nitrogen or steam in order to moderate the reaction.

The life of the catalyst was approximately 45 hr., after which time the activity fell off rapidly. Reactivation could not be accomplished by heating at 400° C. in a stream of air or oxygen nor by treatment with concentrated nitric acid, but heating for one hour at 150° to 175° C. in a solution of 1 part concentrated nitric acid and 10 parts concentrated sulphuric acid regenerated

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Contribution from the Research Laboratories, Dominion Rubber Company Limited, Guelph, Ont.

[2] *Research Chemist.*

the catalyst. This treatment however dissolved a small amount of the platinum surface so that after three or four reactivations most of the platinum black disappeared and a new surface had to be laid by electrolytic deposition.

Experimental

Preparation of the Catalyst

Into a small beaker containing a solution of ammonium chloroplatinate (0.2 gm.) and a trace of lead acetate (about 0.01 gm.) in water (100 cc.) was introduced a sheet of 52 mesh platinum gauze (diameter 0.004 in.) about 4 by 10 in. weighing 20.35 gm., and a piece of platinum foil about 1 by 1½ in. The foil in cylindrical form placed at the centre of the beaker was connected to a positive terminal of a four-volt battery and the gauze surrounding the foil and about ½ in. away from it was connected to the negative terminal through a variable resistance and an ammeter. The resistance was adjusted so that a current of 0.1 amp. flowed through the circuit. After about 20 min. the current was interrupted, the platinum gauze turned inside out, and the plating continued for another 20 min. In this way a uniform adherent surface of platinum black was obtained. It was washed with water, placed on top of a sheet of somewhat heavier copper gauze equal to its own size, rolled up to make a cylinder 4 in. long, and inserted into the catalyst chamber between two rolls of copper gauze.

Apparatus

The catalyst chamber consisted of an electrically heated vertical glass tube ¾ in. in internal diameter and 2 ft. long with a 24 : 40 male ground glass joint at the lower end, a 29:42 female ground joint at the upper end and an outlet tube, about 4 in. below the female joint, connected to a long condenser. This chamber was charged first with a close-fitting roll of copper gauze about 9 in. long, then the prepared catalyst, and finally with a roll of copper gauze 6 in. long. Into the top ground joint was inserted a glass stopper through the middle of which was sealed a thermometer well reaching right into the centre of the platinum catalyst. The temperature of the catalyst could thus be measured by means of a long thermometer or a thermocouple. The bottom ground joint of the catalyst chamber was fitted into one neck of an electrically heated 500 cc. three-necked flask acting as a preheater. Through another neck ethyl lactate was introduced dropwise by means of a siphon containing a grooved stopcock for rate control. The third neck was connected to a Drierite-packed tower, which was connected to a flask receiving air and nitrogen each through separate flowmeters from compressed sources.

Oxidation of Ethyl Lactate

The temperature of the preheater was raised to 200° C. and that of the catalyst to 190° C. by adjusting the resistances of the heaters, and air, nitrogen, and ethyl lactate were introduced into the system at 5 to 5.5 litres per hr., 4.5 litres per hr., and about 4 gm. per hr., respectively. After a few hours of operation the oxidation was initiated, as evidenced by the rise in temperature of the catalyst and by the appearance of two phases (water and ethyl pyruvate) in the distillate. During the oxidation, the temperature of the catalyst was maintained at 200° to 230° C. and that of the preheater at 200° C. After 42½ hr. of continuous operation, the catalytic activity began to fall off, as evidenced by a drop in temperature and a decrease in the amount of ethyl pyruvate in the distillate. During this time 154 gm. of ethyl lactate had been fed into the preheater, 149.7 gm. of distillate was collected, and 15.0 gm. (mostly water) was caught in a dry-ice trap. To the distillate was added sodium chloride (1 gm.) in order to aid in the separation of the two layers, and the water layer (26.4 cc.) was removed. To the organic layer an equal volume of chloroform was added and then distilled off together with a small amount of water that was still present in the organic layer. The residual ethyl pyruvate distilled at 144° to 147° C., yielding 103 gm. (68%) of a colourless liquid, $n_D^{20} = 1.4065$, and a small amount of higher-boiling residue. When 0.50 gm. of the distillate was treated with excess semicarbazide hydrochloride and potassium acetate it yielded 0.63 gm. of semicarbazone, melting at 208° to 209° C. The same amount of pure ethyl pyruvate, prepared by esterification of pyruvic acid (5) and purified by fractional distillation, when treated under the same conditions, yielded 0.65 gm. of semicarbazone melting at 208° to 209° C.

Regeneration of the Catalyst

The platinum catalyst was removed from the reaction chamber, separated from the copper gauze, placed into a solution of concentrated nitric acid (10 cc.) and concentrated sulphuric acid (100 cc.), and heated at 150° to 175° C. by means of an oil-bath for one hour. Then it was removed from the acid, washed well with hot water and replaced in the reaction chamber as before. At this stage the life of the catalyst was usually longer than that of the freshly platinized surface.

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CALYCANTHINE

V. ON CALYCANINE[1]

By Léo Marion[2], Richard H. F. Manske,[3] and Marshall Kulka[4]

Abstract

A compound having the structure previously suggested for calycanine has been synthesized. It is a lepidyl-carboline but is not identical with the degradation product from calycanthine. As an alternative structure for calycanine its formulation as a carboline is abandoned and it is suggested that it is a compound formed by fusion of a carbazole and a pyridine nucleus.

Manske and Marion (8) have submitted a tentative structural formula for calycanthine, and, as a consequence of this formula, have suggested a possible structure (I) for calycanine, one of the degradation products of the alkaloid. In the meantime Hargreaves (6) has subjected calycanine to an X-ray investigation and came to the conclusion that the suggested formula of the former authors cannot obtain. Nevertheless the compound of the given formula has been synthesized. It was found to be quite distinct from calycanine. Not only does it melt some 80° C. lower than calycanine, but, in common with most carboline derivatives, it is intensely fluorescent in neutral or acid solutions while calycanine is not or only slightly so. It is therefore unlikely that calycanine is a derivative of carboline.

Superficially no serious obstacle to the synthesis of a substance of formula (I) was to be anticipated. Claisen (2) reported that propargaldehyde condenses with one mole of aniline in the cold and that when the resulting 1-anilino-2-propyn-1-ol is heated with aniline hydrochloride in aqueous solution malondianilide is formed. Analogously an attempt was made to condense propargaldehyde first with *o*-aminoacetophenone and then to condense the resulting 1-(*o*-acetylanilino)-2-propyn-1-ol with tryptamine hydrochloride. The resulting malondianilide derivative on ring closure and elimination of one mole of water should yield a dihydro-derivative of (I). However an attempt to condense 1-(*o*-acetylanilino)-2-propyn-1-ol with tryptamine hydrochloride resulted in a resinous product only. It was then assumed that the condensation of tryptamine with lepidine-3-carboxylic acid would yield the

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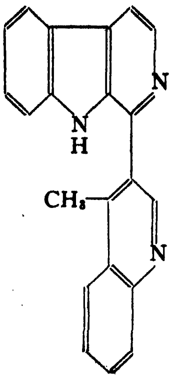
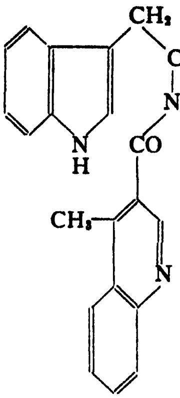


(I)



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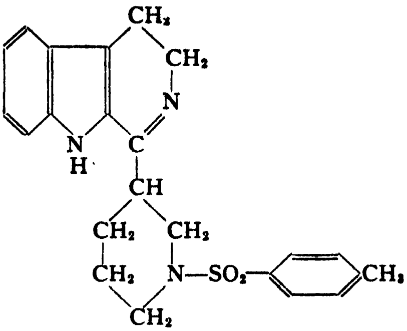


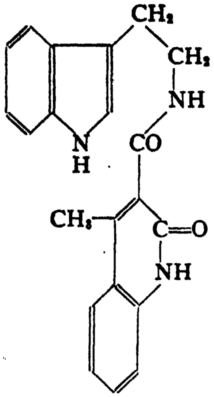
(III)

β-(3-indolylethyl) amide of lepidine-3-carboxylic acid (II) and usual condensing agents used in such cases (phosphorus pentachloride, phosphorus oxychloride, phosphorus pentoxide, etc) would effect ring closure to the dihydroderivative of (I), which in turn could be readily dehydrogenated to (I). These attempts, however, failed. In a parallel case in which the acid moiety was nicotinic acid, ring closure of the amide again failed. It was then recognized that these amides are still bases and that the condensing agents form addition compounds with them which are unreactive. In a pilot experiment, nicotinic acid was first reduced to its hexahydro-derivative (nipecotic acid) (7), which was converted into its *p*-toluenesulphonyl derivative (4). The acid chloride of the latter was condensed with tryptamine and the resulting amide treated with phosphorus oxychloride in chloroform. Ring closure occurred in the normal manner and the piperidyl-carboline derivative (III) was obtained in good yield.

Hydrolysis of (III) occurred when it was heated with 20% hydrochloric acid to yield 3-(3-piperidyl)-5,6-dihydro-4-carboline. The last named compound could not be dehydrogenated successfully by heating with platinum black at 270° C. nor by heating under reflux in tetralin with a little palladium black in a nitrogen atmosphere. In each case low-boiling materials and undistillable neutral resins were formed, indicating degradation.

Attempts to prepare a tetrahydro- or perhydro-lepidine-3-carboxylic acid failed. Reduction occurred but no homogeneous product could be isolated. Attempts to prepare a *p*-toluenesulphonyl derivative of the crude acid likewise failed. Attention was therefore directed to condensing the chloride of 2-lepidone-3-carboxylic acid with tryptamine but the acid could not be converted into its acid chloride.

Ultimately a nucleus synthetic procedure was adopted for the preparation of the required amide (IV). An excess of malonic ester was heated with tryptamine to yield the tryptamide of carbethoxyacetic acid. The latter was condensed with *o*-aminoacetophenone, yielding (IV). Ring closure of this



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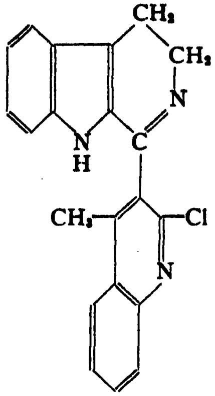
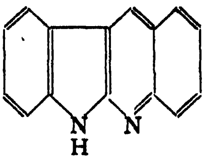


(V)



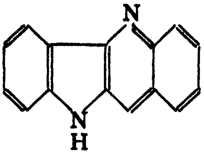
(VI)

compound with phosphorus oxychloride yielded the chloro-compound (V). The elimination of the chlorine and the removal of two hydrogen atoms from (V) to yield (I) was almost quantitatively achieved by heating the substance with palladium black in tetralin in an atmosphere of nitrogen.

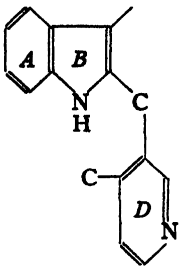
Lepidine-3-carboxylic acid does not appear to have been described. It was obtained from 3-cyano-2-lepidone (1) via the corresponding chloro-compound, namely, 2-chloro-3-cyano-lepidine. The latter was reduced to 3-cyanolepidine with chromous chloride and ultimately hydrolysed to the desired acid.

Having disposed of the suggested structure of calycanine, it becomes expedient to re-examine the known evidence in the hope that a rational formula can be proposed. If the assumption is made that the compound is not a carboline derivative, the source of the basic nitrogen must be sought in a pyridine nucleus. The presence of an active hydrogen suggests an indol nucleus but since the Ehrlich colour reaction is negative, it must be substituted in positions 2 and 3. Since molecular weight determinations yield anomalous results, it is impossible to state with certainty its molecular magnitude. The X-ray investigations already referred to point to two nitrogens or a multiple thereof. The choice is therefore almost certainly limited to $C_{15}H_{10}N_2$. The formula $C_{16}H_{10}N_2$ is abandoned. The analytical figures given by Manske and Marion agree better with $C_{15}H_{10}N_2$ than with any other formula containing two nitrogens. (Found: C, 82.57; H, 4.65; N, 12.64%. Calc. for $C_{15}H_{10}N_2$: C, 82.55; H, 4.59; N, 12.85%).

The fusion of an indol nucleus with a benzene and a pyridine nucleus requires $C_{15}H_{10}N_2$, and, since a carboline seems to be excluded, the order of fusion must be that given, that is, the compound might be one formed by the fusion of a carbazole and a pyridine nucleus. No such substances appear to be known at present although quinindoline (VI) (3), which has two of the nuclei interchanged, has solubility and melting point (342° C.) properties similar to calycanine. The isomeric quinindoline (VII) (5) melts at 247° C. and its solutions are fluorescent. Angular analogues do not appear to be known.



(VII)



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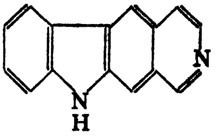

(IX)

There are 12 possible ways in which a carbazole and a pyridine nucleus may be fused. As a working hypothesis certain assumptions may be made. If it is assumed that pyrolysis of calycanthine eliminates all but rings *A*, *B* and *D* of the proposed structural formula, the skeleton (VIII) may remain. Reorientation and ring closure could lead to (IX), which is considered to be one of the more probable expressions for calycanine.

Experimental

1-(o-Acetylanilino)-2-propyn-1-ol

To 5% sulphuric acid (20 cc.) was added 1.75 gm. propargaldehyde diethyl acetal, the mixture heated to 60° C. and then shaken in a stoppered flask until cool. The heating and shaking were repeated several times until complete solution resulted (about one-half hour). The acid solution was neutralized with solid sodium bicarbonate and then a solution of *o*-aminoacetophenone (1.8 gm.) in ethanol (20 cc.) was added. The yellow needle-like crystals that appeared during the course of one hour (1.8 gm., 70%) were filtered, washed with water and dried, m.p. 128° to 131° C.*; recrystallized from benzene and from ether–ethanol, m.p. 135° to 136° C. Calc. for $C_{11}H_{11}O_2N$: C, 69.84; H, 5.86; N, 7.43%. Found: C, 70.03, 69.74; H, 5.62, 5.76; N, 7.55, 7.53%.

Nicotinic Tryptamide

A solution of nicotinic acid (2.5 gm.), dry pyridine (4 cc.), and thionyl chloride (10 cc.) was heated under reflux for one hour. The excess thionyl chloride was removed under reduced pressure, the residue dissolved in a solution of dry chloroform (15 cc.) and pyridine (4 cc.), and a solution of tryptamine (3.0 gm.) in chloroform (15 cc.) added. The resulting reaction mixture was heated under reflux for one hour, the solvent removed under reduced pressure, and to the dark oily residue 50 cc. of warm 4 *N* hydrochloric acid was added. On cooling, the sparingly soluble hydrochloride of nicotinic tryptamide (3.5 gm.) crystallized as yellow needles, m.p. 141° to 142° C. with decomposition. The hydrochloride was dissolved in a minimum amount of hot water and basified with ammonium hydroxide. The oily material that precipitated soon solidified and on recrystallization from benzene containing a little acetone yielded 3.0 gm. (56%) of white microscopic crystals, m.p. 150° to 151° C.; recrystallized from ether containing a little ethanol, m.p. 151° to 152° C. Calc. for $C_{16}H_{15}ON_3$: C, 72.45; H, 5.66; N, 15.85%. Found: C, 72.27, 72.39; H, 5.91, 6.08; N, 15.82, 15.72%.

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* *All melting points are corrected.*

N-p-Toluenesulphonylhexahydronicotinic Tryptamide

To N-*p*-toluenesulphonylhexahydronicotinic acid (12 gm.) (4) dissolved in dry chloroform (50 cc.) was added thionyl chloride (25 cc.) and the solution heated under reflux for one hour. The solvent and excess reagents were removed under reduced pressure and the light-yellow residue was dissolved in chloroform (100 cc.); pyridine (12 cc.) was added and then a solution of tryptamine (8 gm.) in chloroform (100 cc.). A white precipitate of pyridine hydrochloride appeared immediately. The reaction mixture was refluxed for one-half hour, cooled, washed with dilute hydrochloric acid, with dilute ammonium hydroxide and with water, and the solvent removed. The residual oil which would not crystallize was dissolved in boiling benzene and on cooling yielded white microscopic crystals (10 gm., 56%) m.p. 173° to 174° C., recrystallized from benzene and from ether, m.p. 174° to 175° C. Calc. for $C_{23}H_{27}O_3N_3S$: C, 64.94; H, 6.40; N, 9.88%. Found: C, 65.30, 65.27; H, 6.14, 6.14; N, 9.76, 9.67%.

3-(N-p-Toluenesulphonyl-3-piperidyl)-5,6-dihydro-4-carboline (III)

N-*p*-Toluenesulphonylhexahydronicotinic tryptamide (1.35 gm.) was dissolved in dry chloroform (30 cc.), phosphorus oxychloride (6 cc.) added, and the resulting solution heated under reflux for two hours. The light-yellow precipitate was filtered off, washed with chloroform, dissolved in methanol containing a little concentrated hydrochloric acid, water added, and the solution basified with ammonium hydroxide. The cream-coloured precipitate was filtered off, washed with water and dried, yield, 1.0 gm. (80%), m.p. 236° to 237° C., recrystallized from benzene–petroleum ether, m.p., 236.5° to 237.5° C. Calc. for $C_{23}H_{25}N_3O_2S$: C, 67.78; H, 6.19; N, 10.31%. Found: C, 68.15, 67.79; H, 5.95, 5.90; N, 10.32, 10.54%.

3-(3-Piperidyl)-5,6-dihydro-4-carboline

To 3-(N-*p*-toluenesulphonyl-3-piperidyl-5,6-dihydro-4-carboline (III) (2.0 gm.) was added 20% hydrochloric acid (150 cc.) and the reaction mixture heated under reflux until solution was complete (about 45 hr.). The solution was treated with charcoal, filtered, and the filtrate basified with strong sodium hydroxide solution. The white precipitate was filtered, washed, dried, and recrystallized from acetone, and from methanol, m.p. 195° to 196° C.; yield, 1.0 gm. (80%). It was necessary to heat this compound at 144° C. under a pressure of 1 mm. in order to drive off all the solvent. Calc. for $C_{16}H_{19}N_3$: C, 75.86; H, 7.55; N, 16.60%. Found: C, 75.59, 75.86; H, 7.22, 7.14; N, 16.45, 16.53%.

2-Chloro-3-cyano-4-methylquinoline

3-Cyanolepidone-2 (12 gm.) (1) was added to freshly distilled phosphorus oxychloride (60 cc.) and the reaction mixture heated on the steam-bath for one hour. After it was heated under reflux for seven minutes, most of the excess phosphorus oxychloride was removed under reduced pressure and the residue stirred with water (150 cc.) for a few minutes with cooling. The aqueous suspension was made alkaline with sodium hydroxide and the pink-coloured solid (13 gm.) filtered off, washed with water and air-dried; recrystallization from methanol yielded (11.4 gm., 86%) white needles, m.p. 147° to 148° C. There was no change in melting point when the product was recrystallized from ether. Calc. for $C_{11}H_7N_2Cl$: C, 65.18; H, 3.48; N, 13.82; Cl, 17.53%. Found: C, 64.87, 64.72; H, 3.41, 3.40; N, 13.55, 13.72; Cl, 17.7, 17.8%.

2-Methoxy-3-cyano-4-methylquinoline

2-Chloro-3-cyano-4-methylquinoline (0.3 gm.) was dissolved in methanol (25 cc.), sodium (0.3 gm.) added, and the solution heated under reflux for two hours. The methanol was partially removed, water added, and the white needles (0.2 gm., 68%) filtered, washed, and dried, m.p. 118° to 119° C.; recrystallized from methanol, m.p. 120° to 121° C. Calc. for $C_{12}H_{10}ON_2$: C, 72.73; H, 5.05; N, 14.14%. Found: C, 72.62, 72.71; H, 4.89, 5.14; N, 14.16, 14.18%.

3-Cyano-4-methylquinoline

To a solution of chromic chloride hexahydrate (132 gm.) in concentrated hydrochloric acid (400 cc.) was added amalgamated zinc (140 gm.), and the reduction allowed to continue under an atmosphere of nitrogen until complete, as evidenced by a change in colour from green to blue (several hours). The reaction mixture containing the chromous chloride was decanted into a flask previously swept out with nitrogen and containing 2-chloro-3-cyano-4-methylquinoline (12 gm.). The flask was stoppered and allowed to stand at room temperature for 40 hr. Then it was heated under reflux for one-half hour, cooled, diluted with an equal volume of water, and made alkaline with 30% sodium hydroxide. The precipitate was filtered off, washed, and dried at 45° C. Both the filtrate and precipitate were extracted with boiling benzene, the latter with ten 400 cc. portions. The extracts were combined and the benzene distilled off. The tarry residue was shaken with 10% sulphuric acid (200 cc.) and the insoluble tar filtered off. The acid filtrate was basified and the resulting precipitate (7.7 gm.) filtered, washed, and dried; recrystallization from methanol yielded white needles (5.5 gm., 56%), m.p. 140° to 141° C. This material distilled at about 155° C. (6 mm.), and the distillate, recrystallized from methanol, showed no change in melting point. Calc. for $C_{11}H_8N_2$: C, 78.57; H, 4.76; N, 16.67%. Found: C, 78.61, 78.79; H, 4.94, 4.86; N, 16.53, 16.43%.

3-Carboxy-4-methylquinoline

3-Cyano-4-methylquinoline (7.5 gm.) was added to a solution of sodium hydroxide (10 gm.) in water (40 cc.) and ethanol (80 cc.) and the mixture heated under reflux until no more ammonia was evolved (six to eight hours). The reaction mixture was taken almost to dryness under reduced pressure, the residue dissolved in water (75 cc.), and the solution treated with 20% sulphuric acid until just slightly acid to congo red. The white solid (7.6 gm., 90%) was filtered, washed, and dried, m.p. 224° to 229° C. with decomposition; recrystallized from water containing a little acetic acid and from methanol, m.p. 232° to 233° C. with decomposition (rate of heating 4° C. per min). Calc. for $C_{11}H_9NO_2$: C, 70.59; H, 4.81; N, 7.49%. Found: C, 70.78, 70.96; H, 4.93, 4.86; N, 7.27, 7.33%.

Tryptamide of 3-Carboxylepidone-2 (IV)

A solution of tryptamine (5 gm.) and ethyl malonate (20 gm.) was heated under gentle reflux (temperature remained at 150° to 160° C. and finally rose to 195° C.) for 30 min. in a flask fitted with a steam-heated condenser. The excess ethyl malonate was removed under reduced pressure and to the residual oily crude malonic ester amide *o*-aminoacetophenone (4.5 gm.) was added. The resulting solution was heated to 190° to 200° C. and kept at that temperature for one-half hour, the volatile products of the reaction (ethanol and water) being allowed to distil off through a steam-heated condenser. The reaction mixture, which solidified to a hard cake, was pulverized and washed well with cold methanol, yielding 4.8 gm. (40%) of white solid, m.p. 280° to 286° C. insoluble in dilute acids, sodium hydroxide, benzene, acetone, and ethyl acetate, and soluble in glacial acetic acid; recrystallized from butanol, m.p. 285° to 287° C. Calc. for $C_{21}H_{19}O_2N_3$: C, 73.03; H, 5.55; N, 12.17%. Found: C, 73.09, 73.35; H, 5.16, 5.36; N, 11.92, 11.61%.

3-(2-Chloro-3-lepidyl)-5,6-dihydro-4-carboline (V)

To the tryptamide of 3-carboxylepidone-2 (IV) (3.5 gm.) was added phosphorus oxychloride (50 cc.) and the mixture heated on the steam-bath for one and a quarter hours. The excess phosphorus oxychloride was distilled off under reduced pressure and to the residue dilute ammonium hydroxide was added. The yellow insoluble solid was filtered, washed with water, dissolved in a solution of ethanol (50 cc.), water (25 cc.), and concentrated hydrochloric acid (10 cc.) and added to water (150 cc.). The solution was treated with charcoal, filtered, the filtrate basified with ammonium hydroxide, and the cream-coloured precipitate (3.0 gm., 85%) filtered, washed, and dried. Recrystallization from benzene and from ethyl acetate yielded white needles, m.p. 215° to 216° C. Calc. for $C_{21}H_{16}N_3Cl$: C, 72.92; H, 4.66; N, 12.15; Cl, 10.28%. Found: C, 72.77, 72.83; H, 4.56, 4.64; N, 12.04, 12.16; Cl, 10.20, 10.60%.

3-(3-Lepidyl)-4-carboline (I)

A mixture of 3-(2-chloro-3-lepidyl)-5,6-dihydro-4-carboline (V) (1.8 gm.), tetralin (100 cc.) and palladium dust (0.3 gm.) was heated under reflux for 20 hr. and the hydrogen chloride liberated was determined by sweeping out with nitrogen into a solution of silver nitrate. In six hours 80% of the hydrogen chloride was liberated and in 20 hr. 93%. The tetralin solution was decanted from the palladium, extracted with dilute hydrochloric acid, and back-extracted with ether. The acid solution was warmed and basified with sodium hydroxide. The cream-coloured precipitate was filtered, washed with water, dried, and distilled; b.p. about 240° C. (1 mm.). The glassy-like distillate (1.2 gm.) was dissolved in benzene, and, on standing overnight, the solution deposited microscopic yellow crystals losing solvent of crystallization at 185° C. (1.0 gm., 63%), m.p. 230° to 231° C. after drying at 114° C. and 1 mm. for several hours. Recrystallization from dilute ethanol yielded white plates sintering at 150° C. after drying at 110° C. and 15 mm. pressure; and melting at 231° to 232° C. after drying at 144° C. and 1 mm. pressure. Calc. for $C_{21}H_{15}N_3$: C, 81.55; H, 4.86; N, 13.58%. Found: C, 81.80, 81.68; H, 4.56, 4.42; N, 13.63, 13.58.

This compound when heated with platinum in an atmosphere of nitrogen at 250° C. for several hours liberated no hydrogen and remained unchanged.

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PARACHOR OF CERTAIN AZOXY AND RELATED AZO COMPOUNDS[1]

By H. E. Bigelow[2] and K. F. Keirstead[3]

Abstract

The parachors of certain azoxy and related azo compounds have been found. Values for the N_2O group have been calculated from the constants of Sugden and from the recalculated values of Mumford and Phillips. In most cases the experimentally determined values agree better with the values calculated from Sugden's data. Possible explanations for anomalous parachors are discussed.

Introduction

Although the parachors of many organic compounds have already been determined (8), relatively few values have been obtained for the azoxy compounds and their derivatives. The parachors of azoxybenzene (7), azoxytoluene (1), *p*-azoxyanisole (5), *p*-azoxyphenetole (5), ethyl azoxyisopropyl ketone (1), azoxyisopropyl isobutyl ketone, 2-azoxy-2-5-dimethylhexane (1), and ethyl 2-methyl-2-azoxypropionate (1) have been determined. Good agreement was found between experimental values and values calculated on the basis of the open structure of N_2O. The purpose of this investigation is to determine the value of the parachors for various azoxy derivatives and related compounds that have been prepared in these laboratories.

From the examination of the data for isomeric substance and of members of homologous series, S. Sugden (1924) showed (7) the parachor to be primarily an additive, and also a constitutive, property. In view of the appreciable contribution made by structural factors, it is evident that the parachor may be used to decide between alternate configurations provided there is an appreciable difference in structural factors. It may be expected that study of the parachors of azoxy compounds would throw some light on the structural problems of these compounds.

Parachor values have been calculated by us from the constants given by Sugden (8) and from our own measurements. In addition, parachor values have been calculated from the recalculated values and "strain constants" given by Mumford and Phillips (4). In most cases the experimentally determined values agree better with the values calculated from Sugden's data.

From the study of the parachors of azoxybenzene, the value for the group N_2O is calculated by Sugden, Reed, and Wilkins (9) to be 66.7. The mean value from the compounds studied here is 59.2.

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TABLE I

VALUE OF N_2O GROUP

	From Sugden's constants	From constants given by Mumford and Phillips
1. *m-m'*-Dibromoazoxybenzene	54.2	48.8
2. *m-m'*-Dichloroazoxybenzene	57.9	53.1
3. *o-o'*-Dichloroazoxybenzene	49.3	44.5
4. *p-p'*-Dichloroazoxybenzene	53.9	49.1
5. *o*-Nitro-*p-p'*-dichloroazoxybenzene	72.3	66.4
6. Trinitro-*m-m'*-dichloroazoxybenzene	70.0	52.5
7. *m-m'*-Dichlor-*o-o'*-dichloroazoxybenzene	59.1	49.5
8. *p*-Nitro-*m-m'*-dichloroazoxybenzene	57.5	51.6
Mean	59.2	51.9

Experimental Part

Densities were determined with a calibrated pycnometer as used by Sugden (8, p. 203), suspended in a bath at a temperature a few degrees above the melting point of the compound. Surface tensions were measured by the method of maximum bubble pressure as described by Sugden (6, 8).

The surface tension (2) is found by this formula:—

$$= A.P.\left(1 + 0.69 \,.\, r_2 \,.\, \frac{gD}{P}\right),$$

where A is an empirical constant characteristic of the apparatus, P is the difference in pressure (dynes) per square centimetre required to liberate bubbles from the two capillaries, g is the acceleration of gravity, D is the density (grams per cubic centimetre) of the melted compound, and r_2 is the radius (in centimetres) of the larger capillary.

The parachor is found by Macleod's equation

$$P = \frac{M\gamma^{\frac{1}{4}}}{D - d}$$

where M is the molecular weight of the compound, γ is the surface tension as determined above, D is the density of the melted compound as above, and d is the density of the vapour. In all determinations the temperature was kept within a few degrees of the melting point. In such cases the value of d is small and is neglected as in Sugden's determination of the parachor of solid compounds (7).

Whenever possible several determinations were made of both the density and the surface tension. In some cases one determination only could be made on account of the limited supply of the sample or on account of the rapid darkening of the bath at high temperatures. Fisher Bathwax showed little darkening below 150° C. At higher temperatures the bath darkened rapidly, finally making it impossible to read the pycnometer.

(1) *m*-*m*′-Dibromoazoxybenzene,
$C_{12}H_8Br_2N_2O$, $M = 356$, m.p. = 111° C.
$D_{4°}^{120°} = 1.672$ $\gamma^{120°} = 39.92$ whence [*P*] −536
$D_{4°}^{117°} = 1.668$ $\gamma^{117°} = 41.44$ whence [*P*] −536
mean [*P*] −536
[*P*] calc. −548.4(S)
−554.7 (M&P)

(2) *m*-*m*′-Dichloroazoxybenzene,
$C_{12}H_8Cl_2N_2O$, $M = 267.2$, m.p. = 97° C.
$D_{4°}^{105°} = 1.296$ $\gamma^{105°} = 38.07$ whence [*P*] −512.3
[*P*] calc. −521.0(S)
−526.7(M&P)

(3) *o*-*o*′-Dichloroazoxybenzene,
$C_{12}H_8Cl_2N_2O$, $M = 267.2$, m.p. = 56° C.
$D_{4°}^{63°} = 1.325$ $\gamma^{63°} = 38.95$ whence [*P*] −503.7
[*P*] calc. −521.0(S)
−526.7(M&P)

(4) *p*-*p*′-Dichloroazoxybenzene,
$C_{12}H_8Cl_2N_2O$, $M = 267.2$, m.p. = 152.7° C.
$D_{4°}^{150°} = 1.250$ $\gamma^{150°} = 33.62$ whence [*P*] −514.6
$D_{4°}^{157°} = 1.270$ $\gamma^{157°} = 33.60$ whence [*P*] −507.2
$D_{4°}^{161°} = 1.265$ $\gamma^{161°} = 32.50$ whence [*P*] −503.6
mean −508.3
[*P*] calc. −521.0(S)
−526.7(M&P)

(5) *o*-Nitro-*p*-*p*′-dichloroazoxybenzene,
$C_{12}H_7Cl_2N_3O_3$, $M = 311.9$, m.p. = 137° C.
$D_{4°}^{140°} = 1.329$ $\gamma^{140°} = 39.53$ whence [*P*] −588.0
$D_{4°}^{140°} = 1.340$ $\gamma^{140°} = 38.02$ whence [*P*] −578.3
$D_{4°}^{143°} = 1.322$ $\gamma^{143°} = 37.69$ whence [*P*] −584.7
mean −583.7
[*P*] calc. −578(S)
−584.8(M&P)

(6) Trinitro-*m*-*m*′-dichloroazoxybenzene,
$C_{12}H_5Cl_2N_5O_7$, $M = 402$, m.p. = 182° C.
$D_{4°}^{188°} = 1.429$ $\gamma^{188°} = 37.25$ whence [*P*] −695.0
[*P*] calc. −692(S)
−701.0(M&P)

(7) *m*-*m*′-Dichloro-*o*-*o*′-dichloroazoxybenzene,
$C_{12}H_6Cl_4N_2O$, $M = 335.9$, m.p. = 147° C.
$D_{4°}^{150°} = 1.392$ $\gamma^{150°} = 35.24$ whence [*P*] −587.9
[*P*] calc. −595.4(*S*)
−605.9(M&P)

(8) *o*-Nitro-*m*-*m'*-dichloroazoxybenzene,
$C_{12}H_7Cl_2N_3O_3$, $M = 311.9$, m.p. = 112° C.
$D_{4°}^{117°} = 1.382$ $\gamma^{117°} = 36.00$ whence [*P*] −553.0
$D_{4°}^{120°} = 1.377$ $\gamma^{120°} = 36.29$ whence [*P*] −556.1
$D_{4°}^{124°} = 1.375$ $\gamma^{124°} = 36.29$ whence [*P*] −557.0
mean −555.3
[*P*] calc. −578.0(S)
−587.8(M&P)

(9) *p*-Nitro-*m*-*m'*-dichloroazoxybenzene,
$C_{12}H_7Cl_2N_3O_3$, $M = 311.9$, m.p. = 145° C.
$D_{4°}^{151°} = 1.374$ $\gamma^{151°} = 39.70$ whence [*P*] −569.8
$D_{4°}^{148°} = 1.377$ $\gamma^{148°} = 39.06$ whence [*P*] −568.0
mean −568.9
[*P*] calc. −578.0(S)
−584.8(M&P)

(10) *m*-Nitro-*p*-nitro-*m*-*m'*-dichloroazoxybenzene,
$C_{12}H_6Cl_2N_4O_5$, $M = 367$, m.p. = 157° C.
$D_{4°}^{165°} = 1.482$ $\gamma^{165°} = 41.03$ whence [*P*] −671.9
$D_{4°}^{164°} = 1.488$ $\gamma^{164°} = 42.32$ whence [*P*] −674.1
$D_{4°}^{160°} = 1.493$ $\gamma^{160°} = 41.62$ whence [*P*] −668.6
mean −671.5
[*P*] calc. −635.0(S)
−642.9(M&P)

(11) Trinitro-*m*-dichloroazoxybenzene,
$C_{12}H_5Cl_2N_5O_7$, $M = 402$, m.p. =165° C.
$D_{4°}^{170°} = 1.482$ $\gamma^{170°} = 38.95$ whence [*P*] −677.7
$D_{4°}^{172°} = 1.482$ $\gamma^{172°} = 37.24$ whence [*P*] −670.2
$D_{4°}^{173°} = 1.505$ $\gamma^{173°} = 39.74$ whence [*P*] −670.8
mean −672.9
[*P*] calc. 692(S)
701.0(M&P)

(12) Hydroxy-*o*-*o'*-dichloro-*m*-*m'*-dichloroazobenzene,
$C_{12}H_6Cl_4N_2O$, $M = 335.9$, m.p. = 128° C.
$D_{4°}^{135°} = 1.455$ $\gamma^{135°} = 39.23$ whence [*P*] −578.1
[*P*] calc. −587.0(S)
−600.5(M&P)

(13) *p*-Hydroxyazobenzene,
$C_{12}H_{10}N_2O$, $M = 198.2$, m.p. = 152° C.
$D_{4°}^{160°} = 1.089$ $\gamma^{160°} = 37.35$ whence [*P*] −466.2
$D_{4°}^{157°} = 1.092$ $\gamma^{157°} = 36.60$ whence [*P*] −446.3
mean −446.4
[*P*] calc. −448.2(S)
−442.1(M&P)

(14) 2,4-Benzene-bis-azophenol,

$C_{18}H_{14}N_4O$, $M = 302.1$, m.p. = 131° C.

$D_{4^\circ}^{137^\circ} = 1.122$ $\gamma^{137^\circ} = 37.16$ whence $[P]$ -664.9

$[P]$ calc. -626.1(S)

-664.2(M&P)

(15) A Trinitro-*p*-*p*′-dichloroazoxybenzene,

$C_{12}H_5Cl_2N_5O_7$, $M = 402$, m.p. = 189° C.

This compound being melted in a bath at 193° C., rapid decomposition set in, ending in a puff of dense black smoke. This compound was prepared by Bigelow and Wasson.

(16) *o*-Nitro-*m*-*m*′-dichloroazoxybenzene,

$C_{12}H_7Cl_2N_3O_3$, $M = 311.9$, m.p. = 116° C.

$D_{4^\circ}^{120^\circ} = 1.666$ $\gamma^{120^\circ} = 45.52$ whence $[P]$ -482.3

$D_{4^\circ}^{121^\circ} = 1.635$ $\gamma^{121^\circ} = 39.61$ whence $[P]$ -478.8

mean -480.5

$[P]$ calc. -578.0(S)

-584.8(M&P)

Discussion

The compounds used in this study were all prepared in these laboratories and the melting point taken with stem correction. In cases of new compounds, they were purified to constant melting point. The structures of compounds (6), (8), (9), (10), (11), (12), (15), and (16) have not been fully established. In some cases the evidence for the position of one or more substitutes is lacking and hence the position of such groups is not indicated in the name. Compounds (6), (8), (9), (10), (11), and (16) were prepared and described by Bigelow and Steeves (2).

The parachor values calculated from the constants given by Sugden (8) and from our own measurements are in good agreement except for compounds (8), (10), (11), and (16). Since the structures of these compounds have not been fully determined, we must consider the possibility that some alternate structure, such as a cyclic structure, would better correspond to the properties of the compound and to its parachor.

Compound (8) is believed to have the nitro group in the ortho position, but unlike similar compounds, it could not be reduced to the corresponding amine.

The anomalous parachor value for compound (10) was probably due to partial decomposition. No unusual signs of decomposition were seen while the compound was melted. However, chromatographic analysis of the material after melting and cooling showed that some decomposition took place during the heating. When Fisher Adsorption Alumina was used as the adsorbent and a mixture of benzene and ethanol as the solvent, the developed chromatogram showed the presence of two dyes: a bright red dye in the upper portion and a yellow one in the lower portion. No adsorption was evident in the case of the compound before melting. The red dye was soluble in water, and was of a straw colour in acid solution; melting point of red dye, 75° to 80° C.; melting point of hydrochloride of red dye, 132° to 135° C.

Chromatographic analysis was also used to study compound (11) after melting. The developed chromatogram showed the presence of red dyes, thus giving evidence for some thermal decomposition. Not enough of the dye was present to permit comparison of its properties with the red dye produced from compound (10).

Compound (16), whose experimentally determined parachor showed the greatest deviation from the calculated value, showed no signs of decomposition when the material after heating was subjected to chromatographic analysis. Instead of being an azoxy compound as originally described by Bigelow and Steeves (2), compound (16) is more likely *p'*-hydroxy-*o*-nitro-*m*-*m'*-dichloroazobenzene. This compound is highly soluble in water to give a yellow solution suggesting an azo compound. It is also soluble in basic solution, indicating the presence of a hydroxy group. However, the azo form alone would not account for the low parachor since this form would have a parachor greater by the value of the semipolar double bond (1.6).

In the opinion of the authors no reliable conclusions can be drawn from the limited data presented in this paper. It is hoped that a further study can be made of a greater variety of azoxy compounds. As shown in this paper, the experimentally determined parachor value may throw doubt upon the structure assigned to a compound as in the case of compound (8).

Two of the compounds showing anomalous parachors, compounds (8) and (16), have a nitro group in the ortho position and a chloro group in the meta position.

Similar peculiarities of ortho substituted compounds are found in the literature. Gibling (3) reports that the parachors of *o*-hydroxy-derivatives of benzaldehyde, methyl benzoate, and *p*-methoxybenzaldehyde are 2 or 3% less than the calculated values, while those of the *m*- and *p*-compounds are more nearly normal. A further study of such compounds may disclose a diminution of molecular volume brought about either by a closer packing of groups within the molecule, or by a decrease in the effective size of one or other of the atoms concerned, as suggested by Mumford and Phillips (4).

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LX. STABILIZING ACTION OF ETHANOL ON STARCH NITRATES[1]

By W. R. Ashford[2], L. M. Cooke[3], and Harold Hibbert[4]

Abstract

Fractional dissolution has been applied to nitrated corn starch with the consequent removal of ethanol-soluble fractions. Hot and cold ethanol-soluble fractions have been removed in this way amounting to from 10 to 25% of the crude nitrate. The ethanol-soluble fractions, consisting of low-molecular weight and low nitrogen-content material, are not stabilized by ethanol The insoluble portion is greatly stabilized as a result of the ethanol treatment.

The insoluble residue left after ethanol treatment of crude starch nitrate possesses good explosive properties, a high nitrogen content, and high stability. The stabilization of starch nitrate by ethanol is shown to be the result of a dual action, namely, (*a*) removal of highly unstable material of low molecular weight and nitrogen content, and (*b*) the conferring of increased stability by some, as yet unknown, mechanism on the insoluble portion.

Discussion

While the stabilizing action of ethanol upon starch nitrate has been described before (7) its mode of action has not been investigated. Methanol also has been described as a stabilizing agent by Berl and Kunze (2). Ethanol treatment of whole starch nitrate was investigated firstly in an attempt to produce a stable product by this means and secondly to discover something about its mode of action.

Starch nitrate, prepared by nitrating dry corn starch with fuming nitric acid according to the method of Will and Lenze (9), was used in these experiments. The nitrate, after receiving stabilizing boils in water, was subjected to extraction with cold ethanol (95%) which resulted in the removal of 8 to 10% of the crude nitrate as soluble material. In some cases further treatments with hot ethanol, acetone–ethanol, and ether (Fig. 1) were applied, resulting in the extraction of 20 to 25% of the nitrate.

In order that solution of a solid substance may occur, solvation forces must overcome the two cohesions (van der Waal's forces) existing between molecules of solute and of solvent respectively. The solute cohesion in the case of a polymer is determined by the shape and length of the chain, and is usually

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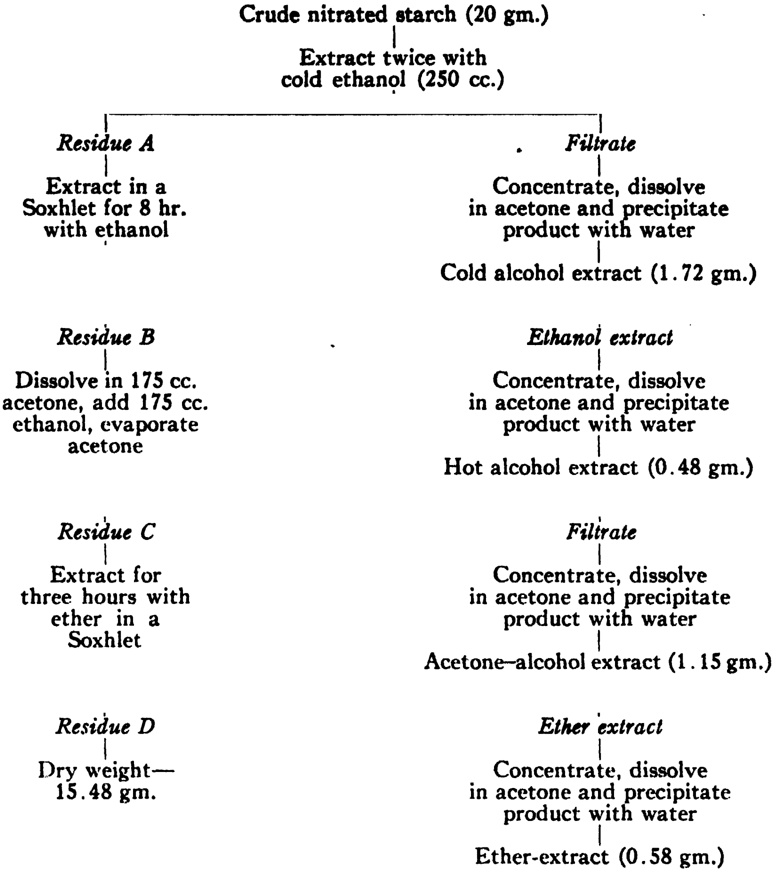
FIG. 1. FRACTIONAL DISSOLUTION OF WHOLE STARCH NITRATE


Crude nitrated starch (20 gm.)
Extract twice with cold ethanol (250 cc.)
Residue A
Extract in a Soxhlet for 8 hr. with ethanol
Filtrate
Concentrate, dissolve in acetone and precipitate product with water
Cold alcohol extract (1.72 gm.)
Residue B
Dissolve in 175 cc. acetone, add 175 cc. ethanol, evaporate acetone
Ethanol extract
Concentrate, dissolve in acetone and precipitate product with water
Hot alcohol extract (0.48 gm.)
Residue C
Extract for three hours with ether in a Soxhlet
Filtrate
Concentrate, dissolve in acetone and precipitate product with water
Acetone–alcohol extract (1.15 gm.)
Residue D
Dry weight— 15.48 gm.
Ether extract
Concentrate, dissolve in acetone and precipitate product with water
Ether-extract (0.58 gm.)

much smaller for branched chain polymers than for the linear chain type; the latter are therefore much more soluble. The extent of solvation is also determined by the chemical nature of the groups attached to the polymer chain, especially in relation to the chemical structure of the solvent.

The fractional dissolution method was fully developed and tested first with cellulose nitrate (11.4% N) by Rogowin and Glasman (8) who claim important advantages for the method over the technique employing fractional precipitation. One disadvantage of the dissolution method, however, is that solute and solvent are not in complete and intimate contact, i.e., the process involves a heterogeneous system.

The solubility of a nitrated starch depends upon (i) its chain length, (ii) its degree of association and the power of the solvent to break hydrogen bonds, and (iii) the nitrogen content. At the end of the nitration reaction, there is present a heterogeneous mass of varying chain lengths, degrees of association, and nitrogen contents. Thus the use of fractional dissolution for the fractionation of starch nitrate permits a separation based on both physical and chemical properties. Shorter, non-associated chains, especially those of lower nitrogen content, are removed, leaving a product that may be visualized as a micellar mass formed of tightly interlocking chains. The amount of this residual product will depend upon the dissociating power of the solvent used. With 95% ethanol, the residue constitutes about 90% of the crude nitrate (Residue *A*, Fig. 1).

The characteristics of the ethanol-insoluble fraction and ethanol-soluble fraction are given in Table I. Here the results of the fractionation of two different nitrates are given. The nitrate described in experiment No. 1 resulted from a nitration period of seven hours while the nitrate described under experiment No. 2 was produced by nitrating for a period of 24 hr. The effect of this longer nitration period is readily noticeable in the specific viscosities of the two nitrates. Apparently the longer nitration period caused considerably more degradation of the starch molecules. The nitrogen content of the readily extractable fractions was, in all cases, lower than that of the residual products, being about 8 to 9% in the various ethanolic fractions investigated. Viscosity determinations on the ethanol-soluble fractions (Table I) showed considerable variation in molecular complexity. The lower specific viscosity is not surprising since shorter chains show greater solubility in ethanol and in solvents generally.

TABLE I

CHARACTERISTICS OF PRODUCTS OBTAINED FROM WHOLE STARCH NITRATE BY FRACTIONAL DISSOLUTION

Fraction	N content, %*	η_{sp}, specific viscosity†	Abel value, min.
Expt. No. 1 . . . . Starch nitrated for 7 hr.			
Cold ethanol extract	9.1	0.1910	—
Hot ethanol extract	8.81	0.5777	—
Acetone–ethanol extract	10.55	0.8129	—
Residual product (*D*, Fig. 1)	13.43	—	55
Residual product: (*D*, Fig. 1)	Ignition point—183° C. Brown fumes —165° C.		
Expt. No. 2 . . . . Starch nitrated for 24 hr.			
Cold ethanol extract	8.89	0.0357	—
Acetone–ethanol extract	10.63	0.4050	—
Residual product	13.96	0.509	30
Residual product:	Ignition point—185° C. Brown fumes —173° C.		

* *N content determined by ferrous sulphate method (3) checked by Dupont nitrometer (4, pp. 401-423).*

† *Specific viscosity determined by capillary flow method (5) in acetone at 25° C.*

The ethanol-soluble portion of all starch nitrates examined was found to have a lower stability than the residual product as judged by the Abel test (Table II).

TABLE II

STABILITIES OF PRODUCTS FROM FRACTIONAL DISSOLUTION OF STARCH NITRATE

Fraction	Abel stability, min.
Unfractionated nitrate	3
1. Cold ethanol extract	3
2. Hot ethanol extract	7
3. Acetone–ethanol extract	25
4. Ether extract	20
5. Residual product (*D*, Fig. 1)	40

The residual product (*D*, Fig. 1) from different nitrates examined had Bergmann–Junk values ranging from 2.27 to 2.97 mgm. of nitrogen evolved, while samples of unfractionated nitrate were so unstable under the conditions of this test that in some instances the test could not be applied. Thus, in the case of whole starch nitrate, ethanolic extraction with consequent removal of low-molecular weight material results in an appreciable increase in stability. The maximum instability allowed commercially in the case of cellulose nitrate is that corresponding to an evolution of 1.25 mgm. of nitrogen per gram of sample.

The residual product (*D*, Fig. 1) from the ethanol treatment of starch nitrate, which proved to be of good stability by means of the Abel and Bergmann–Junk tests, was subjected to (*a*) the ignition, (*b*) the machine impact, and (*c*) the Trauzl lead block tests (Table III).

In the ignition test, brown fumes appeared at a lower temperature (about 170° C.) than in the case of cellulose nitrate (182° C.). Also, the actual ignition temperature was about 5 degrees lower. The machine impact test indicated a sensitivity some two to three times greater than that of trinitrotoluene. The Trauzl lead block test showed a net expansion of 358 cc. as compared with trinitrotoluene, 254 cc.; nitroglycerine, 540 cc.; tetranitromethylaniline, 375 cc.; dynamite, 300 cc.; and cellulose nitrate, 290 cc. (1, pp. 179-181).

From the above results, it is evident that starch nitrate contains unstable components of low molecular weight and nitrogen content which are readily extractable by cold ethanol. These components (Table II) are not stabilizable by treatment with ethanol as is the main body of the nitrate (Table III). Thus ethanol presumably functions in a dual capacity, namely, as an extractant for certain unstable portions of starch nitrate and as a stabilizer for the higher molecular-weight material.

TABLE III

EXPLOSIVE CHARACTERISTICS OF ETHANOL-INSOLUBLE STARCH NITRATE

Moisture, %	Ignition temperature		Machine impact test		Sensitivity times T.N.T. T.N.T. = 1	%N*	Abel test, min.
	Ignites, ° C.	Brown fumes, ° C.	Hammer drop, cm.	Hammer drop, % T.N.T. = 100%			
	Residual product, Expt. 1, Table I.						
0.68	183 with flame	167	44	27.5	3.64	13.43	55
	Residual product, Expt. 2, Table I.						
0.55	185 with flame	173	58	36.2	2.76	13.96	30
Trauzl lead block test (50% of each product). Net expansion—358 cc. Net expansion, T.N.T. Standard—256 cc.							

* *N content by Dupont nitrometer (4, pp. 401-423).*

Experimental

Nitration

The nitration procedure of Will and Lenze (9) was followed with modifications. A typical nitration procedure is as follows. Concentrated nitric acid (sp. gr. 1.5, 1200 cc.) in a three litre, three-necked flask, fitted with a stirring motor, was placed in a brine bath at a temperature of −7° C. Unmodified corn starch (120 gm.) was added to the mixture over a period of 45 min., during which time the mixture was stirred vigorously, and the temperature maintained at −7° C. Nitration was completed by continuing the stirring in nitric acid for a period of six hours at the same temperature and then adding concentrated sulphuric acid (600 cc.) over a period of one and one-half hours. The nitrated starch was isolated by pouring the nitration mixture on to vigorously stirred, finely chopped ice and the product separated by filtration. It was washed on the filter with large quantities of cold distilled water, placed in a three-necked flask fitted with a reflux condenser, and boiled for at least 150 hr. using two changes of water, one after 50 and the second after 100 hr., respectively. At the end of this period, the product was filtered and an aliquot portion cautiously dried and weighed. Yield, 204 gm. or 170%*.

Fractional Dissolution of Whole Starch Nitrate

Ethanol (95 to 98%) was used as the solvent in these fractional dissolution studies. The nitrated starch was dried (at 55° C.), prior to treatment, as the presence of more than 5% water greatly reduces the solubility of nitrated starch in ethanol. Ethanolic extraction was carried out by suspending the starch nitrate (20 gm.) in ethanol (250 cc.) and stirring the mixture vigorously at room temperature for three hours, the process being twice repeated. In most cases, it was necessary to grind the nitrate in ethanol in a mortar in order to remove lumps. The undissolved residue was separated by filtration.

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* *% yields are based upon the theoretical value for starch nitrate (182.7 gm. from 100 gm. starch).*

The ethanolic extract was concentrated to small volume (50° C., 20 to 25 mm.) until the dissolved nitrate precipitated. Precipitation was completed by the addition of petroleum ether. The nitrate was separated by filtration and petroleum ether removed by drying at 50° C. The product was then boiled with water (2 litres) under reflux for 15 to 20 hr. to ensure removal of the ethanol. The insoluble residue was treated in a similar manner. About 8 to 10% of the total nitrate was removed in this way.

The extraction of starch nitrates with ethanol was extended in certain cases to include further extractions as recommended by Will and Lenze (9). The procedure was as follows (Fig. 1). Nitrated starch (20 gm.) was extracted by stirring at room temperature with two portions of ethanol (250 cc., 98%) for periods of three hours. The undissolved residue was removed by centrifuging and then extracted for a period of eight hours in a Soxhlet, using ethanol as the solvent. The residue left after this treatment was dissolved in acetone and an equal volume of ethanol (98%) added to the mixture. When the acetone was removed under reduced pressure, the nitrated starch precipitated from the remaining ethanol. The solution and residue were separated by centrifugation. The dried product remaining from the acetone–ethanol treatment was then extracted for three hours with diethyl ether in a Soxhlet. The residue was placed in three litres of distilled water and boiled at reflux temperature for 20 hr. to remove traces of solvent. A small aliquot portion was dried (55° C.) and the remainder left in the wet condition until needed.

The various ethanolic extracts obtained by cold ethanol extraction, hot ethanol extraction, and by acetone–ethanol treatment were each concentrated at 50° C. (20 to 25 mm.) to small volume. Each precipitated nitrate was dissolved in a small quantity of acetone and precipitated by the addition of water. The products were washed by boiling with water at reflux temperature.

Determination of Nitrogen Content

Nitrogen contents were obtained using a modified Bowman–Scott method (3) and the Dupont nitrometer method (4, pp. 401-423). The Bowman–Scott method was carried out as follows.

(*a*) *Preparation of Reagents*

Standard nitric acid was prepared of such strength that 1 cc. of the solution contained approximately the same quantity of nitrogen as a sample of starch nitrate weighing 0.05 gm. and containing 12.5 to 13.0% nitrogen. Standard ferrous sulphate ($FeSO_4 . 7H_2O$) solution was prepared of such strength that about 5.0 cc. of the solution was equivalent to 1 cc. of the above standard nitric acid solution when used according to the conditions of the Bowman–Scott method. The nitric acid and ferrous sulphate solutions usually employed were 0.45 N and 0.25 M respectively. The strength of the ferrous sulphate solution was determined in terms of grams of nitrogen per cubic centimetre, before each set of analyses by titration against a standard nitric acid solution in the following manner. A 1 cc. sample of standard nitric acid was added slowly and with cooling to concentrated sulphuric acid (25 cc.). The samples were then placed in an ice-bath, and in turn titrated to a permanent end-point (colourless to pinkish-brown) with standard ferrous sulphate solution. The equivalence of 1 cc. of ferrous sulphate solution in grams of nitrogen is given by the expression .

$$\frac{1}{1000} \times \frac{\text{Normality } HNO_3 \times 14}{\text{cc. } FeSO_4 \text{ used.}}$$

(b) Determination of Nitrogen

The samples were dried at 63° C. for a period of three hours in an Abderhalden apparatus. Duplicate samples of about 0.05 gm. were weighed out and dissolved in 25 cc. of concentrated sulphuric acid at room temperature. The samples were then titrated as described above.

Determination of Stabilities

(*a*) *The Abel Heat Test*

All essential features of the standard Abel test were included in the procedure followed (6, pp. 644-660). The important modification was the introduction of thermostatic control to maintain a temperature of 76.7° C. (170° F.). The bath used consisted of a metal container about 12 in. deep and 10 in. in diameter with a tightly fitting, removable lid. The outside surface of this vessel was surrounded by several layers of asbestos. Through separate orifices in the lid there were fitted a strong mechanical stirrer, a thermoregulator and a knife-edge heater. These fixtures were held in place by tightly fitting rubber stoppers so that the vessel, when sealed, was steam tight. In addition, the lid was provided with six openings, each fitted with a one-holed rubber stopper of such size as to accommodate the standard Abel test-tube. The temperature of the water in the bath was raised to about 75° C. by means of a Bunsen burner and then increased to the required 76.7° C. by means of the knife-edge heater, and maintained at this value by means of the thermoregulator, which was of the usual type (filled with mercury and carbon tetrachloride).

Tests were carried out in duplicate using 0.5 gm. samples. These were first dried at 63° C. in an Abderhalden for one hour, then allowed to stand in an open dish at room temperature at a relative humidity of 55 to 65%. This ensured a moisture content of about 1%. The starch–iodide papers were standardized by testing a known sample of cellulose nitrate. The starch–iodide test paper was held in position in the Abel test-tube by means of a hooked glass rod inserted through a rubber stopper. After use, these glass hooks and rubber stoppers were boiled for a few minutes in a dilute solution of sodium hydroxide (0.5%) and then in distilled water. They were then dried at 50° C. on a piece of clean filter paper.

(*b*) *The Bergmann–Junk Test*

The nitrated starches were tested for stability by means of the Bergmann–Junk test using 0.5 gm. samples instead of the 2.0 gm. samples prescribed in the official test. Cellulose nitrate samples (0.5 gm.) were used as a standard. These Bergmann–Junk tests were carried out by the Department of Mines and Resources, Explosives Division, Ottawa, Canada.

Acknowledgments

The authors wish to thank the Canada Starch Co. for providing the starch used in these experiments and Mr. M. C. Fletcher, Chief Explosives Chemist, Department of Mines and Resources, Ottawa, under whose direction certain of the explosive tests reported herein were carried out by Dr. A. Gillies.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

LXI. PROPERTIES OF THE FRACTIONATED NITRATES OF TWO FRACTIONS OF CORN STARCH[1]

By W. R. Ashford, T. H. Evans, and Harold Hibbert

Abstract

Corn starch has been separated into two individual components, arbitrarily designated as amylose (linear fraction) and amylopectin (branched-chain fraction) by means of preferential adsorption on cellulose (Tanret–Pacsu method). These components have been nitrated and their nitrates fractionated by dissolution in ethanol. The relative stabilities and nitrogen contents of the nitrated fractions have been studied.

Unfractionated amylose nitrate has greater stability than unfractionated amylopectin nitrate as judged by the Bergmann–Junk test. Dissolution methods of fractionation showed a much higher solubility of the amylopectin nitrate, the greater relative stability of the amylose fractions, and the somewhat greater stabilizing action of ethanol in the case of the latter.

The widely different solubilities of amylose and amylopectin nitrates in conjunction with the lower ethanol solubility of whole starch nitrate are in accordance with the theory of a branched-chain structure for amylopectin and the linear type for amylose.

Introduction

Most of the earlier work (from 1833 on) on starch nitrate is concerned with methods of preparation, stabilization, and use in explosives, but no exhaustive investigation has been made with the object of providing a satisfactory explanation of its abnormal instability. Application of the customary procedures by which cellulose nitrates are stabilized proved of little or no value in the case of starch nitrates. The former are known to be essentially stable following removal of acidic and ester-type impurities.

The heterogeneity of all varieties of starch is apparent from the work of recent investigations (13, pp. 166-170) and it is to be expected that the nitrates of starch should be still more heterogeneous. The heterogeneity of cellulose is in one direction only, namely, in the matter of varying chain lengths, there being no tendency toward the formation of branched chains as with starch. With the former, the long chains are united laterally essentially by "hydrogen bonding" to give the crystalline micelle, whereas in starch only a small part of the total granule (the amylose) may have this type of structure.

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Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, Montreal, Que. From a thesis presented to the Faculty of Graduate Studies and Research, McGill University, by W. R. Ashford in May 1943 in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

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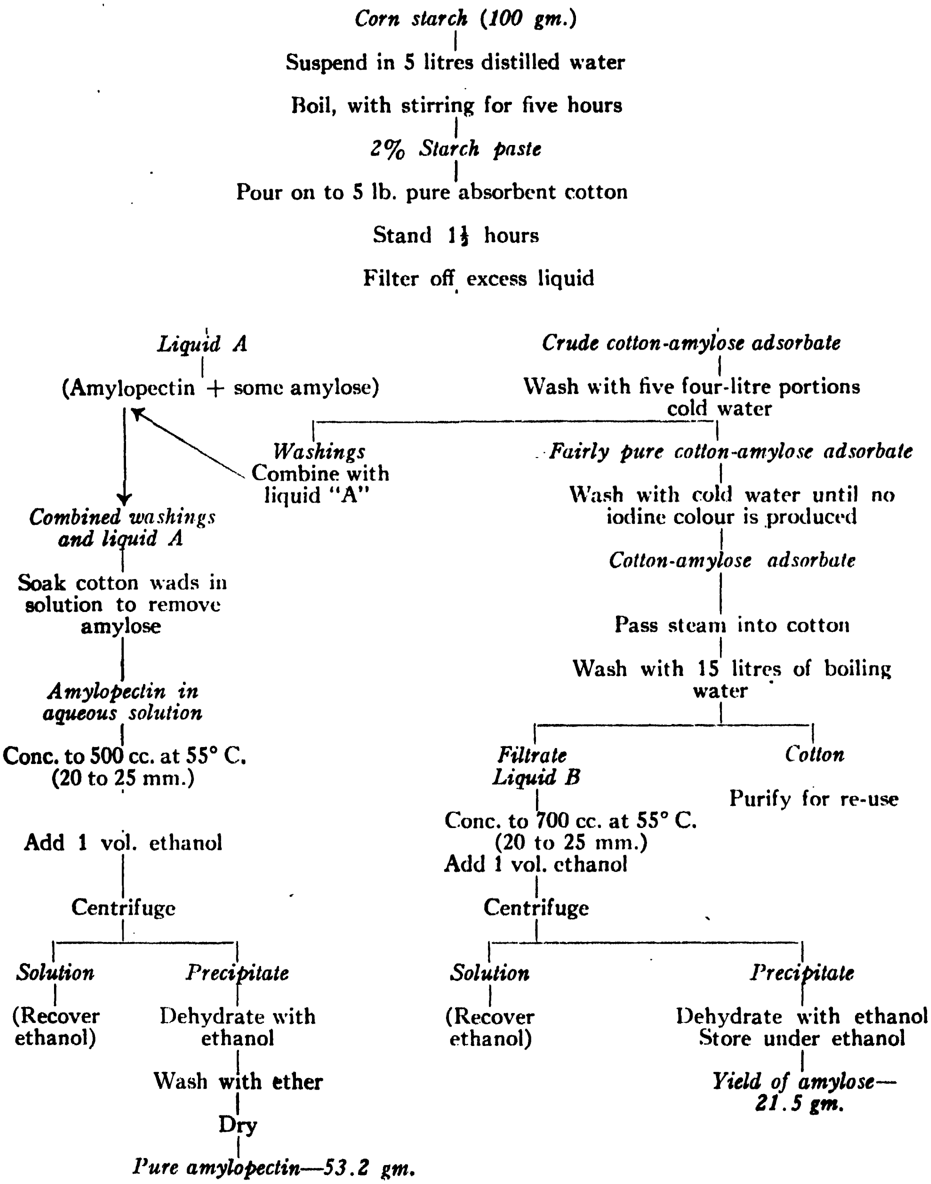
It was evident that no definite conclusions on starch nitrate stability was possible prior to a careful investigation of the properties of the nitrates prepared from the amylose and amylopectin portions of the starch granule (13, pp. 166-170), especially in view of recent improvements in methods of their isolation. This seemed all the more desirable in that, although much work has been done on the fractionation of cellulose nitrates (20), only little attention has been paid to the fractionation of starch nitrates. Berl and Kunze (3), using a freezing technique, separated starch nitrate into two components, which they claimed were amylose and amylopectin nitrates, respectively. Centola (5) separated amylose and amylopectin nitrates on the basis of their solubilities in ethanol, while the same principle was employed by Snelling (19) to obtain three fractions from whole starch nitrate.

Several methods have been used in an attempt to fractionate starch into its separate components and thus achieve some elucidation of its structure. These include precipitation of amylopectin from starch pastes by use of salts of the alkaline earths (24), treatment with superheated steam (15), treatment with water at 75° to 90° C. (8), centrifugation (7, 18), Ling and Nanji's freezing technique (2, 11), electrodecantation (6, 16, 22), ultrafiltration (22), and selective adsorption (14, 21). Two more recent methods of fractionation are those of Schoch (17, pp. 247–275) and a modification of same by Kerr (8; 9, pp. 129–178). The former is based on the selective precipitating action of *n*-butanol toward starch sols, two products of markedly different physical and chemical characteristics being obtained. The second method is similar except that the precipitant consists of a mixture of *n*-butanol and methanol. All methods employ swelling agents of various kinds which may bring about hydrolysis of the glucosidic linkages so that the products isolated may not be the true constituents of native starch. The selective adsorption method avoids the use of harsh swelling reagents and employs activated carbon, Fuller's earth, or cotton cellulose for the preferential adsorption of the amylose. The work herein described was carried out using the selective adsorption method (Fig. 1) with cotton cellulose as the adsorbent. The cotton-amylose adsorbate is formed instantaneously when a cold corn starch paste (2%) is brought into contact with cotton and can be washed free of amylopectin by cold water. The adsorbate is then readily decomposed by boiling water to give a clear solution of amylose. The dissolved amylose can be converted to the solid form by concentration of the solution followed by precipitation with alcohol.

The purpose of this fractionation of corn starch was to obtain, if possible, homogeneous products suitable for nitration, and the characteristics of the nitrates obtained indicate that this was accomplished to a considerable degree. In order to make possible a more thorough study of the properties of two of the components of starch (amylose, amylopectin) a fractionation of the nitrates of these two components was undertaken and a study made of the characteristics of the resulting products. To this end, fractional dissolution was employed. This method makes use of the different solubility characteristics exhibited by fractions of different molecular weight and chemical constitution. Such fractions are usually present in high polymeric substances, especially those of natural occurrence, e.g., starch.

FIG. 1. FRACTIONATION OF STARCH BY THE ADSORPTION PROCESS


Corn starch (100 gm.)
Suspend in 5 litres distilled water
Boil, with stirring for five hours
2% Starch paste
Pour on to 5 lb. pure absorbent cotton
Stand 1½ hours
Filter off excess liquid
Liquid A
(Amylopectin + some amylose)
Crude cotton-amylose adsorbate
Wash with five four-litre portions cold water
Washings
Combine with liquid "A"
Fairly pure cotton-amylose adsorbate
Wash with cold water until no iodine colour is produced
Combined washings and liquid A
Soak cotton wads in solution to remove amylose
Cotton-amylose adsorbate
Pass steam into cotton
Wash with 15 litres of boiling water
Amylopectin in aqueous solution
Conc. to 500 cc. at 55° C. (20 to 25 mm.)
Add 1 vol. ethanol
Centrifuge
Solution
(Recover ethanol)
Precipitate
Dehydrate with ethanol
Wash with ether
Dry
Pure amylopectin—53.2 gm.
Filtrate
Liquid B
Conc. to 700 cc. at 55° C. (20 to 25 mm.)
Add 1 vol. ethanol
Centrifuge
Solution
(Recover ethanol)
Precipitate
Dehydrate with ethanol
Store under ethanol
Yield of amylose—21.5 gm.
Cotton
Purify for re-use

The solubility of a nitrated starch depends upon (i) its chain length, (ii) its degree of association and the power of the solvent to break associative bonds, and (iii) the nitrogen content. At the end of the nitration reaction there is present a heterogeneous mass of varying chain lengths, degrees of association, and nitrogen contents. The use of fractional dissolution for the fractionation of starch nitrates permits a separation based on both physical and chemical properties. Shorter, non-associated chains, especially those of lower nitrogen content, are removed, leaving a product that may be visualized as a micellar mass formed of tightly interlocking chains. The dissolution method has the disadvantage that the process involves a heterogeneous system.

The following analytical methods were employed for the characterization of the nitration products.

(*a*) *Nitrogen Content*

Determinations of nitrogen content were made by two methods: (i) the Bowman–Scott method (4) using certain modifications; and (ii) the Dupont nitrometer method (10, pp. 401–423).

(*b*) *Determination of Stability of the Nitrates*

Many tests have been devised to measure the stability of the nitrated polysaccharides of the nitrocellulose type of explosive (12, pp. 644–660). In most of these the heat stability of the product under examination is measured. In the present investigation, the two most widely used tests, namely, the Abel heat test and the Bergmann–Junk test, have been employed. It is generally assumed that the Abel test indicates the physico-chemical condition of an explosive from the point of view of the ease of decomposition that may exist owing to the presence of minute amounts of foreign substances. The main objection to the Abel test is its extreme sensitiveness, the standard tint being produced by as little as 0.000135 mgm. of nitrogen peroxide. In the present work, the technique of the Abel test was simplified and all precautions taken (1). The heat test values obtained are therefore considered to represent the amount of impurity present in the sample at the time of the test and to indicate the initial stages of decomposition.

In contrast to the Abel test the Bergman–Junk test is quantitative and is not affected to nearly the same extent by added adulterants. Furthermore, it indicates the stability that may be expected over a long period of storage, since the products of decomposition are left in contact with the nitrate during the entire heating period. This test is also dependent upon the moisture content of the sample and is influenced by the presence of certain impurities such as urea.

The Bergmann-Junk test as applied to starch nitrates was modified in one respect only, namely, the size of sample used. Instead of the customary 2.0 gm. sample, amounts weighing 0.5 gm. were used and compared for stability with a similar quantity of cellulose nitrate.

The nitrates of amylose and amylopectin after subjection to fractional dissolution gave rise to products of varying nitrogen content, Abel heat value and Bergmann–Junk stability (Table I).

It is significant that 86.7% of the amylopectin nitrate was ethanol-soluble, whereas only 20% of the amylose nitrate was dissolved by the alcohol. A

TABLE I

FRACTIONAL DISSOLUTION OF AMYLOSE AND AMYLOPECTIN NITRATES AND CHARACTERISTICS OF THEIR PRODUCTS

Product	Weight, gm.	% of crude product	% N	Abel heat value	Bergmann–Junk*, mgm. of N_2
Amylose nitrate	60.0	100	12.96	10	7.28
Ethanol-insoluble amylose nitrate	46.0	79.5	13.28	40	2.62
Ethanol-soluble amylose nitrate	12.3	20.5	11.62	55	1.90
Amylopectin nitrate	60.0	100	12.25	4	15.20
Ethanol-insoluble amylopectin nitrate	6.9	13.3	12.58	16	3.74
Ethanol-soluble amylopectin nitrate	52	86.7	11.82	13	2.23

* *Mgm. of nitrogen evolved per 1.0 gm. sample of nitrate.*

high stability (Abel) was found with both the soluble and insoluble amylose nitrate fractions, those of the corresponding amylopectin nitrates being less stable. Prior to testing, all traces of ethanol were carefully removed by repeated boiling in distilled water, drying, and extraction with petroleum ether. The Bergmann–Junk tests confirmed these Abel heat test results in that the amylose nitrates had a higher stability than the amylopectin nitrates. It is of interest that the treatment of crude amylopectin and amylose nitrates with ethanol in the fractionation process actually brought about an increase in the stability of both the alcohol-soluble and alcohol-insoluble fractions.

In a previous paper dealing with whole starch (1) it was found that only about 10 to 20% of the whole starch nitrate could be extracted by use of ethanol as a solvent, whereas, as pointed out above, amylopectin nitrate treated independently with ethanol is 86% soluble and the amylose nitrate about 20% soluble. One explanation for this is that in the case of the whole starch nitrate, the solvent is unable to break associative bonds necessary for solution, while, when the amylopectin is separated from the amylose, associative bonding is greatly lessened and solution of the former component can take place more readily.

Amylose nitrate is no more soluble than whole starch nitrate because it is responsible for the associative bonding in whole starch. This conclusion is based upon a highly branched structure for amylopectin and a linear, non-branched structure for amylose or, conversely, the solubility results herein reported can be taken as evidence for the branched and non-branched structures for amylopectin and amylose, respectively.

In the paper referred to above (1), the problem was to obtain, if possible, a stable starch nitrate, either by removal of unstable fractions by ethanol solution or by the stabilizing action of ethanol. That it would be extremely difficult or impossible to remove the less stable portions of starch nitrate by ethanol dissolution is evident from the results herein reported, when it is observed, first, that those less stable portions consist of amylopectin nitrate which, by present theories, constitutes about 75% of the starch molecule, and second, that only 10 to 20% of whole starch nitrate was found to be ethanol-soluble.

The fact that fractional dissolution in ethanol did bring about increased stability in starch nitrate would seem to indicate that the 10 to 20% of material removal by ethanol dissolution was mainly amylopectin nitrate.

Experimental

Fractionation of Corn Starch

Corn starch (100 gm.) was added to five litres of distilled water and the mixture boiled for five hours to ensure complete rupture of the granules (Fig. 1). Five pounds of pure absorbent cotton was introduced into the starch solution and allowed to stand for one and one-half hours at room temperature. The paste-soaked cotton was then placed in a large earthenware filter and the liquid remaining from the five litres of starch solution removed by suction filtration. The filtrate (Liquid *A*) was reserved for future work. The cotton was washed with five four-litre portions of cold distilled water, and the wash waters added to the original filtrate. The cotton was washed with further portions of cold, distilled water until the filtrate gave no colour with iodine, indicating absence of amylopectin. The cotton was then subjected to live steam, while still on the filter, and suction applied. The hot, moist cotton was treated repeatedly with boiling water, using a total of about 15 litres, in order to remove the adsorbed amylose. The filtrate (Liquid *B*) gave a bright blue colour with iodine. The absorbent cotton can be used repeatedly.

Liquid *B*, containing the amylose fraction, was concentrated to about 700 to 800 cc. at a bath temperature not exceeding 55° C., and the amylose precipitated quantitatively by the addition of an equal volume of ethanol. The product was separated by centrifuging as a fine, white precipitate and was readily dehydrated by the use of 80% ethanol followed by a further centrifuging and by grinding under absolute ethanol. The final product, a white powder, was stored in ethanol to prevent drying and consequent retrogradation. Yield of dry product (calculated by drying an aliquot portion) was 21.5 gm.

Liquid *A*, the amylopectin fraction, was freed from amylose by adsorbing the latter on pieces of cotton. When a hot water extract of a piece of cotton, which had been washed with cold water, no longer gave a blue iodine colour reaction, the complete removal of amylose was indicated. The 20 litres of solution were then concentrated at 50 to 55° C. (20 to 25 mm.) to 500 cc. The addition of an equal volume of ethanol caused precipitation of a flocculent, sticky mass of amylopectin. The product was centrifuged and dehydrated with ethanol, washed with ether, and dried in a desiccator. Yield, 53.2 gm.

Nitration of Amylose and Amylopectin

(*a*) *Preparation of nitric acid.*—Colourless nitric acid (98.6%) was prepared as required by distillation (60 to 70° C., 20 to 30 mm.) from a 1:1 mixture of nitric (1.42 sp. gr. or commercial fuming nitric) and concentrated sulphuric acids (1.84 sp. gr.) in an all ground-glass set up.

(*b*) *Nitration procedure.*—Nitrations were carried out according to the Will and Lenze method (23) as described previously (1). Yields amounted to 160 to 170% for amylose and amylopectin (% yields are based upon the theoretical value for starch nitrate (182.7 gm. from 100 gm. starch)).

Fractional Dissolution of Amylose and Amylopectin Nitrates

Sixty grams of each nitrate was placed in a litre of ethanol (98 to 99%) and stirred for a period of 10 hr. at room temperature, and the residue separated by centrifuging and filtration. The ethanolic extract in each case was evaporated to small volume (30 to 35° C., 20 to 25 mm.). In the case of the amylopectin extract, the nitrate was precipitated by the addition of petroleum ether (30 to 50° C.) and in the case of the amylose extract by the addition of water. The extracted nitrates were placed in two litres of distilled water and the solution boiled under a reflux condenser for 12 hr. in order to replace the solvent. In similar manner, the residues left undissolved by ethanol were treated by boiling in water for 12 hr. to remove ethanol. Weights and proportions of the two fractions are shown in Table I.

Nitrogen Content and Stabilities

These two characteristics of the nitrated products were determined as outlined in a previous paper (1). Their values are given in Table I.

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LIQUID–VAPOUR EQUILIBRIUM FOR THE SYSTEM ETHANOL–ACETONE[1]

By A. R. Gordon[2] and W. G. Hines[3]

Abstract

Vapour pressures and equilibrium liquid–vapour mole fractions have been determined for the solvent system ethanol–acetone at 32°, 40°, and 48° C. in a modified form of the apparatus developed by Ferguson and Funnell. It is shown that the data are consistent with the Gibbs–Duhem equation if it be assumed that deviations from ideality in the vapours may be computed from the principle of Corresponding States. It is also shown that the variation of the activities of the components in the liquid with temperature is in moderate agreement with the heat of mixing data for the system.

The work reported here was undertaken to provide liquid–vapour equilibrium data for the important solvent system ethanol–acetone. The majority of such studies reported in the literature have involved some sort of distillation procedure. The possible sources of error in such measurements are now well understood—superheating of the liquid, lack of equilibrium between liquid and vapour, reflux in the apparatus, entrainment of droplets of liquid in the vapour given off, etc.; the elaborate modification of the familiar Sameshima apparatus used by Scatchard and Raymond (11) in their study of the system ethanol–chloroform is an example of the precautions to be taken if accurate results are to be obtained. In 1929, Ferguson and Funnell (2) reported a novel and much improved form of the apparatus developed by Rosanoff *et al.* (8, 9); in a closed all-glass system, the vapour was continuously circulated through the liquid until equilibrium was attained, the vapour and liquid phases were separated, the vapour condensed, and both phases analysed; the apparatus used here is a modification of theirs, and (we believe) an improvement on it.

There is an additional complication with the system ethanol–acetone since analysis by refractive index or density is not practical, while chemical methods are excluded if reasonable accuracy is desired. The compositions of the liquid and condensed vapour were therefore determined by measuring their vapour pressures, previous independent measurements having fixed the vapour pressure curve for the system. Under the most unfavourable conditions (low temperature and high acetone concentration) a precision of 0.1 mm. of mercury corresponds to 0.08 mole % in the composition, and under the most favourable to about one-sixth of this.

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Experimental

The apparatus is shown in Fig. 1. Essentially, it consists of a bulb *A*, of approximately 75 cc. capacity, containing the liquid phase, and immersed in a covered water thermostat regulated to 0.002° C.; the vapour is circulated through the liquid in *A* by the all-glass, electrically operated Funnell–Hoover (3) pump *P*, thence through the small bulb *B* and finally through the large bulb *D* (of 13 litres capacity). The vapour part of the apparatus is enclosed in a double-walled air-bath whose temperature is held 0.5° C. higher than that of the water-bath; the pump *P* (capacity 12 litres per hr.) is in a separate compartment maintained at a temperature 2° C. higher than that of the main air-bath. The glass tubes running from *A* above water level to the air-bath are thermally shielded by heavy double-walled copper tubes, the space between the tubes being packed with rock wool. *K* indicates a copper box with separate double-walled door, to permit momentary access to this part of the apparatus without disturbing the temperature of the main air-bath. All glass tubing in the apparatus was of 8 mm. internal diameter to ensure rapid circulation of the vapour. The levelling line *L* of the manometer was viewed through a double glass window, while the manometer scale *M* was of silvered plate glass, ruled by the dividing engine in the Physics Department of this University, and checked by microscope comparator. Not shown in Fig. 1 is a small glass jar enclosing the bulb *B* and connected to the main water-bath by a siphon; a very small electric heater in the jar maintains the temperature of *B* during a run slightly above that of *A*. Bath temperatures were read on Beckmann thermometers set against laboratory standards that had been calibrated by means of a platinum resistance thermometer with National Bureau of Standards certificate.

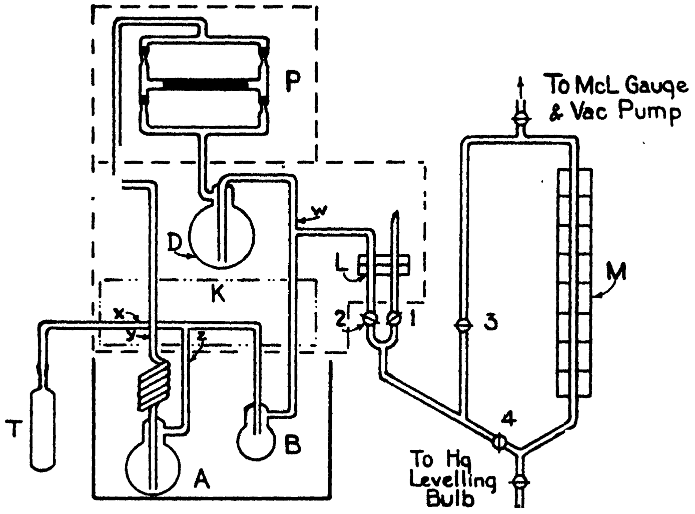

Fig. 1.

In carrying out a measurement, usually from 20 to 30 gm. of an ethanol-acetone solution was placed in the filling tube *T*, which was fitted with a standard taper joint; the sample was then frozen with liquid air. With the mercury in the manometer just above tap 4, and with taps 2 and 3 open, the apparatus was evacuated; tap 3 was then closed, the sample melted and frozen again, and any air resulting pumped off. This was repeated, usually three or four times, until the residual pressure after melting and freezing was not greater than 0.001 mm. as measured on the McLeod gauge. The sample was then distilled into *A*, frozen with liquid air, and *T* was sealed off with a burner at *x*. The air-bath was brought on temperature, the mercury raised to the level *L*, tap 3 was closed, and the vacuum reading on the manometer scale *M* was taken. The air-free sample was thus enclosed in an all-glass apparatus in which the vapour was not in contact with any stopcock and in which the only mercury–glass contact, that at *L*, could be maintained, with proper manipulation, practically stationary throughout the experiment.

The water-bath was then filled and brought on temperature, and the pump started. When constancy of pressure had shown that equilibrium had been attained (this usually required from four to six hours) the pump was stopped and the equilibrium vapour pressure was read; after circulating the vapour for another 30 min., a second reading was taken with *P* stopped, and after a further 30 min., a third; to be accepted the three successive readings had to agree within 0.1 mm. The pump was then stopped, and the bulb *A* was sealed off from the rest of the apparatus at *y* and *z*, thus separating the liquid and vapour. After draining the water-bath, the vapour was condensed into *B* with liquid air, and *B* was then sealed off from *D* at *w*; after the trace of non-condensable gas had been pumped off, the water-bath was filled and brought on temperature, and the vapour pressure of the condensed vapour was taken.

To interpret such pressure readings in terms of composition, the vapour pressure curve for the system must be known. A weighed sample of gravimetrically known composition (from 20 to 30 gm.) after being outgassed was distilled into a flask similar to *A* with liquid air, the flask then being sealed off from its filling tube; this flask connected directly to the manometer through tap 1. When the water-bath had been filled, the vapour pressure was read after temperature equilibrium had been attained. There is one correction that must be made, however, before such readings may be used to fix the vapour pressure curve. Part of the weighed sample evaporates, and, although the amount is small in comparison with the liquid, its composition is different from that of the liquid whose vapour pressure has been determined, i.e., the composition of the actual liquid will be slightly different from that of the sample distilled into the apparatus. As a first approximation, this was neglected, and a provisional vapour-pressure–liquid-composition curve was drawn; from this and the vapour–liquid equilibrium measurements, a provisional curve of vapour composition as a function of liquid composition was obtained. Since the volume involved in the vapour pressure measurements was known, viz., 212 cc. less the volume of the sample weighed out, it was now possible to make an approximate calculation of the weight and composition of the vapour above the liquid in the vapour pressure measurements and so arrive at the true composition of the liquid whose vapour pressure had been determined. In extreme cases, the true liquid composition differed by as much as 0.3 mole % from that of the sample that had been introduced into the apparatus. From this corrected vapour pressure curve, a corrected liquid-vapour composition curve was obtained, allowance now being made for the vapour above the condensed vapour when the vapour pressure of the latter was read. Calculation showed that a third approximation was not necessary.

The alcohol was 99.5% absolute, refluxed under nitrogen with magnesium and a trace of iodine for 15 hr., and distilled, the first and last fractions being rejected. The acetone was Shawinigan A.R. grade; after refluxing under nitrogen with potassium permanganate for six hours, it was distilled, the middle 60% being retained and redistilled. The final distillate was allowed to stand over anhydrous sodium carbonate for 24 hr., then siphoned through glass wool into a storage flask containing Drierite that had been activated at 140° C. under vacuum for 24 hr.; samples were distilled under vacuum from the storage flask into the weighing tubes. The manometer mercury was acid washed and twice distilled under vacuum.

Results

The vapour pressure measurements are recorded in Table I, and the liquid-vapour equilibrium results in Table II; in the tables P stands for the pressure in millimetres of mercury reduced to 0° C. and N_1 and N_1' for the liquid and vapour mole fractions of acetone respectively. From large-scale deviation plots of these data, values of P and of N_1' were obtained for round values of

TABLE I

VAPOUR PRESSURE MEASUREMENTS

32° C.		40° C.		48° C.	
N_1	P	N_1	P	N_1	P
0	87.6	0	134.2	0	200.8
0.0422	112.5	0.0389	162.1	0.0507	244.7
0.0673	124.4	0.0446	165.1	0.1234	297.2
0.1130	145.2	0.0765	184.0	0.1634	321.8
0.1787	169.3	0.1409	219.1	0.3179	394.5
0.2361	186.1	0.1883	240.1	0.4410	438.9
0.2665	191.9	0.2683	270.3	0.5601	474.3
0.3128	205.4	0.3406	292.8	0.7063	511.6
0.3470	212.8	0.4355	318.5	0.8218	537.9
0.4458	232.8	0.5315	340.6	1.0000	572.3
0.5372	247.8	0.6528	366.0		
0.6548	265.3	0.7727	388.0		
0.7721	281.9	0.8593	402.9		
0.8474	291.7	0.9038	410.2		
0.9252	301.0	1.0000	424.9		
1.0000	309.9				

N_1 and are given in Table III; with very few exceptions, the experimental points from Tables I and II differed from the smooth curves corresponding to Table III by less than 0.2 mm. in the pressure and by less than 0.002 in N_1'.

TABLE II

EQUILIBRIUM LIQUID–VAPOUR COMPOSITIONS

32° C.		40° C.		48° C.	
N_1	N_1'	N_1	N_1'	N_1	N_1'
0.0255	0.1630	0.0265	0.1515	0.0205	0.1005
0.0410	0.2350	0.0285	0.1565	0.0395	0.1770
0.0700	0.3360	0.0520	0.2525	0.0440	0.1960
0.1020	0.4195	0.0875	0.3420	0.0735	0.2850
0.1565	0.5120	0.0955	0.3685	0.1185	0.3830
0.2250	0.5970	0.1395	0.4540	0.1965	0.5035
0.2580	0.6260	0.2215	0.5590	0.2015	0.5090
0.3335	0.6835	0.2640	0.6030	0.2550	0.5615
0.3865	0.7160	0.3260	0.6470	0.3670	0.6500
0.4795	0.7605	0.3710	0.6750	0.5080	0.7375
0.6245	0.8280	0.4745	0.7360	0.6430	0.8085
0.6895	0.8565	0.6200	0.8035	0.7285	0.8525
0.8430	0.9240	0.7565	0.8680		
0.8720	0.9380	0.8735	0.9290		

TABLE III

N_1	32° C.		40° C.		48° C.	
	N_1'	P	N_1'	P	N_1'	P
0	0	87.6	0	134.2	0	200.8
0.025	0.1605	102.7	0.1435	152.2	0.1210	223.3
0.050	0.2700	116.2	0.2460	168.5	0.2155	244.1
0.075	0.3505	128.3	0.3205	183.3	0.2890	263.6
0.10	0.4130	139.7	0.3795	197.4	0.3460	281.6
0.15	0.502	159.5	0.470	223.3	0.437	314.2
0.20	0.569	175.9	0.538	244.9	0.507	341.5
0.25	0.619	190.1	0.590	263.9	0.560	365.5
0.30	0.660	202.4	0.631	280.6	0.602	387.0
0.40	0.722	223.8	0.694	309.0	0.670	424.9
0.50	0.773	242.0	0.747	334.0	0.731	457.4
0.60	0.817	257.4	0.795	355.5	0.785	485.0
0.70	0.859	271.9	0.843	375.1	0.838	510.1
0.80	0.902	285.3	0.893	393.0	0.889	533.0
0.90	0.950	297.9	0.945	409.4	0.942	553.6
1.00	1.000	309.9	1.000	424.9	1.000	572.3

Our vapour pressures for ethanol, viz., 87.6, 134.2, and 200.8 mm. at 32°, 40°, and 48° C. are definitely below those recorded in International Critical Tables (4, p. 217), which correspond for these three temperatures to 88.0, 135.3, and 201.7 mm. respectively. They may be compared with those given by Scatchard and Raymond's corrected equation (12) for the same three temperatures, 87.4, 134.1, and 200.7 mm. The vapour pressures recorded for acetone in the literature are not at all concordant, as has been pointed out by Beare, McVicar, and Ferguson (1); our results for the two lower temperatures agree most closely with those of Price (7) and for 48° C. with that of Sameshima (10).

One check on the self-consistency of the experimental data may be obtained from the familiar Gibbs–Duhem equation. If the customary assumption (justified for the small range of pressures involved) be made that the thermodynamic potentials μ_1 and μ_2 of the acetone and the ethanol in the liquid phase are independent of pressure, then for constant temperature

$$N_1 \,.\, d\mu_1 + N_2 \,.\, d\mu_2 = 0. \tag{1}$$

If the equilibrium vapour be assumed to obey the equation of state

$$P(V - n_1'\beta_1 - n_2'\beta_2) = (n_1' + n_2')RT, \tag{2}$$

where n_1' and n_2' are the moles of acetone and ethanol in the vapour and β_1 and β_2 the corresponding second virial coefficients, it is easy to show (11) that Equation (1) may be written

$$d \ln P = \frac{(N_1' - N_1)}{N_1'(1 - N_1')} \,.\, dN_1' - \frac{(N_1\beta_1 + N_2\beta_2) \,.\, dP}{RT} \,. \tag{3}$$

Thus if the vapour pressure of one pure component and the virial coefficients be known, it is possible by integration and successive approximation to compute the entire vapour pressure curve for the system from a knowledge of the equilibrium liquid and vapour mole fractions.

For neither acetone nor ethanol are vapour density data available of accuracy sufficient to fix the β's; in a similar situation, Scatchard and Raymond (11) appealed to the principle of Corresponding States and in particular to the equation of Keys, Smith, and Gerry (6):

$$\beta(P_c/T_c) = 11.5 - (24.78/T_r) \times 10^{0.1930/T_r^2} \,, \tag{4}$$

where P_c and T_c are the critical pressure and temperature and T_r is the reduced temperature. For acetone, the critical temperature and pressure are 508° K and 47 atm., respectively, while for ethanol the corresponding values are 516° K and 63 atm. (4, p. 248); the resulting values of β_1 and β_2 in cubic centimetres per mole from Equation (4) are

	32° C.	40° C.	48° C.
Acetone	−1405	−1275	−1165
Ethanol	−1130	−1025	− 935

If these values are used in Equation (3), the agreement is not satisfactory; Scatchard and Raymond (11) found the same to be true for the system ethanol–chloroform, and accordingly multiplied both coefficients by the same arbitrary factor for a given temperature, viz., 2.2, 1.65, and 1.5 for 35°, 45°, and 55° C., respectively. This is obviously equivalent to assuming that Equation (4) gives the correct ratio for the coefficients but not their absolute values, and has the advantage that in checking the experimental results by means of Equation (3) there is only one adjustable parameter—the factor r by which the corresponding states β's have been multiplied. Fig. 2 shows the result of the same procedure here; the continuous curves in the figure correspond to the integration of Equation (3) when the values of r selected are 2.7, 1.8, and 1.2 for 32°, 40°, and 48° C., respectively; P_2^0 is the vapour pressure of pure ethanol for the given temperature, corresponding to the lower limit of integration, and the circles indicate the vapour pressures recorded in Table III. The values of r used are of the same order of magnitude as those of Scatchard and Raymond although they decrease more rapidly with rising temperature than do theirs. As the figure shows, the agreement is moderate, in general within 0.005 in the common logarithm, and is probably as close as can be expected in view of the uncertainty as to the equation of state on the one hand, and the precision of the data on the other.

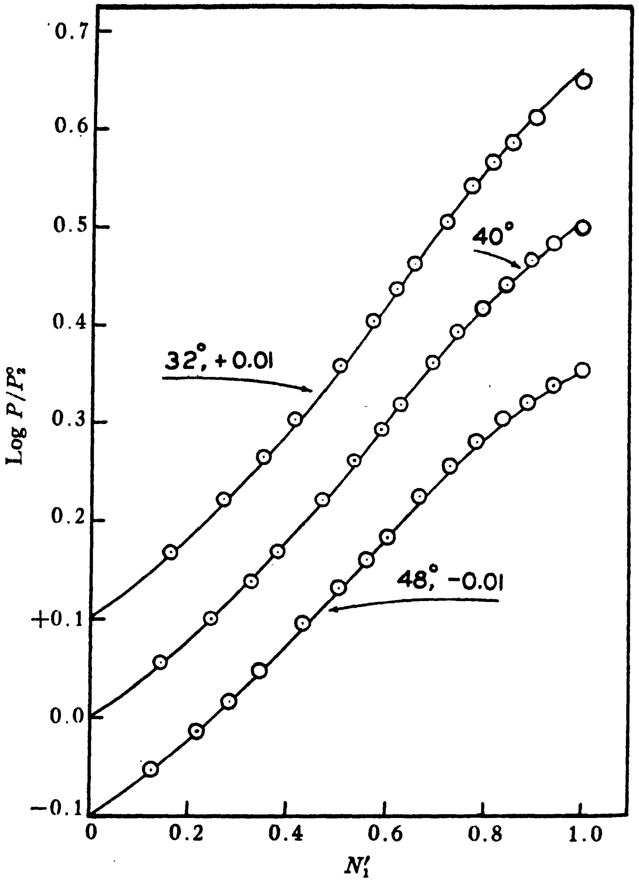

FIG. 2.

There is another check that may be applied to the data. The activity a_1 of the acetone in a solution is given by

$$\ln a_1 = \ln N_1'P/P_1^\circ + r\beta_1(P - P_1^\circ)/RT, \tag{5}$$

where P_1° is the vapour pressure of pure acetone and r is the arbitrary factor by which the corresponding states virial coefficients have geen multiplied; see above. Since

$$\partial \ln a_1/\partial T = (H_1^\circ - H_1)/RT^2, \tag{6}$$

where H_1° is the molal heat content of pure acetone and H_1 is the partial molal heat content of acetone in the solution, it is possible by integration of Equation (6) to calculate the activity at one temperature from the activity in the same solution at another temperature provided $(H_1^\circ - H_1)$ is known for the temperature range. From the heat of mixing data for this system (5, p. 156), it is possible to obtain for 25° C. the values of $(H_1^\circ - H_1)$ and $(H_2^\circ - H_2)$ entered in Table IV. If it be assumed that these are valid for the range 32° to 48° C. (this is obviously equivalent to assuming that the molar heat capacity for ethanol–acetone solutions is linear in the mole fraction) one can obtain at once values of a_1 at 32° C. and at 48° C. from that at 40° C. From this and a similar calculation for a_2, it is then possible, since P_1°, P_2°, and r are known, to solve for N_1' and P by a short series of approximations. The results of such calculations are given in Table IV in the lines labelled N_1' calc. and P calc. A comparison of Table IV with Table III shows that the agreement for N_1' is reasonably satisfactory; in only one instance is the discrepancy greater than 0.5 mole %. The agreement with respect to the pressures is also as close as can be expected except possibly for the solutions low in acetone at 32° C.

TABLE IV

N_1	0.1	0.2	0.4	0.6	0.8	0.9
$(H_1^\circ - H_1)$, cal.	−900	−680	−380	−210	− 60	− 10
$(H_2^\circ - H_2)$, cal.	− 10	− 50	−170	−350	−700	−960
N_1' calc., 32° C.	0.412	0.569	0.717	0.811	0.900	0.948
P calc., 32° C.	137	173	221	256	285	298
N_1' calc., 48° C.	0.349	0.507	0.671	0.780	0.886	0.942
P calc., 48° C.	281	342	425	485	533	554

It would seem safe to say that our results are not inconsistent with the Gibbs–Duhem equation on the one hand and the thermal data on the other. We therefore feel that while the precision of the data may not be as great as one could wish, Table III cannot be very seriously in error.

Acknowledgment

We wish to express our thanks to Dr. E. A. Hollingshead of this Department for his assistance in some of the preliminary measurements.

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LIQUID-VAPOUR EQUILIBRIUM FOR THE SYSTEM ETHANOL–DIETHYL-ETHER[1]

A. R. GORDON[2] AND W. J. HORNIBROOK[3]

Abstract

Vapour pressures and equilibrium liquid–vapour mole fractions for the system ethanol–ethyl-ether have been determined at 25° C. in the apparatus previously employed for the system ethanol–acetone. The measured vapour pressures deviate from those reported in the literature by more than the apparent precision of the measurements. The type of equation of state for the vapour that must be assumed in order to make the data consistent with the Gibbs–Duhem equation is discussed.

In this paper we report vapour pressures and equilibrium liquid–vapour mole fractions for the system ethanol–diethyl-ether at 25° C. Louder, Briggs, and Browne (4) have determined the vapour pressure curve for this system over a range of temperatures, but there is no information in the literature as to the composition of the vapour in equilibrium with a given liquid. This system provides an interesting contrast to that studied in the preceding paper owing to the relatively great difference in the vapour pressures of ethanol and ether.

Experimental

The apparatus, the experimental technique, the method of analysis, the corrections to be applied, and the method of purifying the ethanol have been described in detail (1). The ether was Analar grade; it was first shaken with 50% by weight sulphuric acid, decanted, and shaken with calcium oxide in order to dry it and free it from suspended acid. It was then refluxed with sodium wire in an atmosphere of carefully dried nitrogen until the addition of 1 gm. of benzophenone through the reflux condenser turned the entire liquid blue. The reflux condenser was drained, and the ether was then distilled into its container through a down condenser, care being taken that the atmosphere in contact with the ether at all times was dry nitrogen. It was stored in a two litre balloon flask under a slight positive pressure of dry nitrogen.

Results

The vapour pressure measurements are summarized in Table I and the liquid–vapour composition measurements in Table II. It should be noted that the analysis of the liquid phase and the condensed vapour by means of their vapour pressures is much more sensitive here than in the case of the system ethanol–acetone, particularly for solutions high in ethanol. In the tables, P is the pressure in millimetres of mercury reduced to 0° C., and N

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Contribution from the Chemistry Department, University of Toronto, Toronto, Ont.

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TABLE I

Vapour pressure measurements

N	0	0.0506	0.1018	0.1547	0.2370	0.2874	0.3745
P	58.9	125.7	183.2	232.6	294.3	323.9	365.9
N	0.4338	0.5175	0.6308	0.7958	0.9052	1.0000	—
P	388.6	416.1	446.6	484.1	510.1	535.8	—

TABLE II

Equilibrium liquid–vapour compositions

N	0.0128	0.0322	0.0577	0.1104	0.2239
Y	0.2392	0.4420	0.5860	0.7235	0.8395
N	0.3260	0.5255	0.7710	0.9700	—
Y	0.8775	0.9155	0.9510	0.9918	—

and Y are the mole fractions of the ether in liquid and vapour, respectively. From large-scale deviation plots of the data, the values of Y and P for round values of N, entered in Table III, were obtained. It might be noted in passing that a convenient deviation function, suitable for correlating and interpolating the composition data, is defined by

TABLE III

N	Y	P	N	Y	P
0	0	58.9	0.25	0.852	302.2
0.005	0.1105	66.0	0.30	0.870	330.7
0.01	0.1985	73.1	0.35	0.883	355.4
0.02	0.3305	86.7	0.40	0.893	376.1
0.04	0.4950	112.8	0.50	0.911	410.6
0.06	0.5940	137.3	0.60	0.925	438.9
0.08	0.6600	160.1	0.70	0.939	462.5
0.10	0.7070	181.3	0.80	0.956	485.2
0.15	0.7815	228.5	0.90	0.976	509.2
0.20	0.8245	268.8	0.95	0.988	522.2
—	—	—	1.00	1.000	535.8

$$Y = 0.9860N/(N + 0.0395) + \delta\,, \tag{1}$$

the resulting δ being less than 0.003 for values of N up to 0.35; for the higher ranges of concentration, deviations obtained by subtracting from Y a suitable linear function of N are adequate.

Our measured vapour pressure for pure ethanol at this temperature is somewhat below that given in International Critical Tables (59.0 mm.) and is definitely below that reported by Louder, Briggs, and Browne, viz., 59.7 mm.; it is 0.2 mm. above that given by Scatchard and Raymond's corrected vapour pressure equation (5). Our result for pure ether, 535.8 mm., lies below the International Critical Tables (2, p. 288) value and that of Louder, Briggs, and Browne (537 mm.). A comparison of our values of the vapour pressures for the solutions with those of Louder, Briggs, and Browne shows that for solutions up to 60% by weight (48 mole %) their results lie from 1 to 3 mm. below ours; for their three solutions strongest in ether, however, their values are from 2 to 4 mm. above ours. This eliminates a difference in temperature in the two researches as a cause of the discrepancy, and suggests (as do the vapour pressures of the pure components) that the raw materials used in the two laboratories were different.

A check on the data by means of the Gibbs-Duhem equation

$$N \,.\, d\,\mu_1 + (1 - N) \,.\, d\,\mu_2 = 0\,, \tag{2}$$

where μ_1 and μ_2 are the potentials of the ether and the ethanol in the liquid, requires a knowledge of the equation of state of the vapour. In the absence of vapour density data for the gaseous solutions, the second virial coefficients β_1 and β_2 may be computed, as was done in the case of the system ethanol–acetone, by means of the principle of Corresponding States from the equation of Keyes, Smith, and Gerry (3); see Equation (4) of the preceding paper. The critical temperatures for ether and ethanol are 467° and 516° K, respectively, and the corresponding critical pressures 35.5 and 63 atm. (2, p. 248); the resulting values of β_1 and β_2 are -1367 and -1236 cc. per mole. Integration of the Gibbs–Duhem equation with these values of the coefficients (see Equation (3) of the preceding paper) shows however that the vapour pressure curve calculated from the Y–N data lies *above* the observed vapour pressures. This is in contrast to the system ethanol–acetone where the calculated curve was too low, and a reasonable fit could be achieved by multiplying both the corresponding states β's by a common factor greater than unity. This suggests that the more general equation of state (5)

$$V/(n_1 + n_2) = RT/P + Y\beta_1 + (1 - Y)\beta_2 + Y(1 - Y)\epsilon \tag{3}$$

be employed, where n_1 and n_2 are the moles of ether and ethanol in the vapour, $\epsilon = 2\,\beta_{12} - \beta_1 - \beta_2$, and β_{12} is the cross-virial coefficient. The potential of the ether in the vapour, μ_1', is then given by

$$\mu_1' = \mu_1^{\circ\prime} + RT \ln PY + \beta_1 P + \epsilon(1 - Y)^2 P, \tag{4}$$

where $\mu_1^{\circ\prime}$ is a function only of the temperature, with an analogous expression for the potential of the ethanol. If it be assumed that the potentials in the liquid are independent of pressure, substitution of the expressions (4) in Equation (2) gives

$$d \ln P = \frac{Y - N}{Y(1 - Y)} \,.\, dY - \frac{[\beta_1 N + \beta_2 (1 - N)] \,.\, dP}{RT} - \frac{\epsilon}{RT} \,.\, [N(1 - Y)^2 + (1 - N)Y^2 + 2Y(1 - Y)]\, dP\,. \tag{5}$$

Equation (5) is a simplified form of Scatchard and Raymond's (5) Equation (6) since in obtaining the last term of Equation (5), $2\,(Y-N)\,P\,.\,dY/dP$ has been replaced by its approximate value $2Y\,(1-Y)$, i.e., third order terms have been neglected.

The result of integrating Equation (5) with $\beta_1 = -1367$ cc., $\beta_2 = -1236$ cc., and $\epsilon = 4280$ cc. is shown by the continuous curve of Fig. 1; the circles correspond to the entries in Table III, and P_2° is the vapour pressure of ethanol. The value selected for ϵ corresponds to $\beta_{12} = 840$ cc., a not unreasonable value, and the figure shows that except for the highest points, the agreement between calculated and observed vapour pressure is moderately satisfactory. Not too much stress must be placed on this, however. One would expect, by analogy with the results for ethanol–acetone, that the values of the second virial coefficients computed by Keyes, Smith, and Gerry's equation would be too low. If β_1 and β_2 are both arbitrarily multiplied by 3 (cf. the values of r used in the preceding paper) and ϵ be set equal to 8600 cc., i.e., $\beta_{12} \backsim 400$ cc., the resulting calculated curve is practically indistinguishable on the scale of the figure from the curve as printed. In other words, the use of two adjustable parameters—the arbitrary factor by which corresponding states β's are multiplied, and the value selected for β_{12}—reduces the attempt to check the data by means of the Gibbs–Duhem equation to little more than an exercise in curve fitting. Nevertheless, we believe that the results indicate that an equation of state of the type (3) is more suitable for this system than the simpler form used for ethanol–acetone.

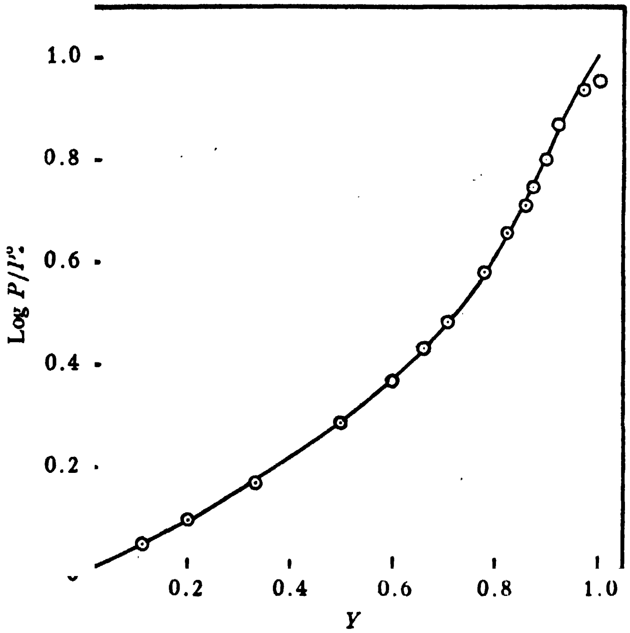

FIG. 1.

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PRODUCTION AND PROPERTIES OF 2,3-BUTANEDIOL

XVI. DENSITY, OPTICAL ROTATORY POWER, AND REFRACTION OF AQUEOUS 2,3-BUTANEDIOL SOLUTIONS[1]

BY K. A. CLENDENNING[2]

Abstract

Addition of water to the *levo-* and *meso-*isomers of 2,3-butanediol increases the specific gravity to a maximum at 50 to 60% diol, beyond which it is gradually reduced. Contraction on mixing is strongly influenced by temperature and is slightly greater with the *levo-* than with the *meso-*isomer. The coefficient of thermal expansion for the *levo-*isomer is higher than that of the *meso-*form. Water exerts a pronounced influence on the specific rotation value of the *levo-*isomer, reducing it from −13° (anhydrous) to approximately −9° for solutions containing 40 to 70% water; on further dilution, the specific rotation value rises. With increase in temperature, the optical rotatory power of the anhydrous *levo-*isomer is reduced, whereas that of 30 to 90% aqueous solutions is increased. Refractive index data are provided for aqueous *meso-*2,3-butanediol solutions at 25° C. and for aqueous *levo-*2,3-butanediol solutions at 20°, 25°, 30°, and 35° C. From several lines of evidence it is concluded that the hydration tendencies of the two isomers are approximately equivalent.

Introduction

Aqueous solutions of *meso-* and *levo-*2,3-butanediol exhibit remarkable differences in freezing point at identical glycol concentrations (2, 4). Corresponding dissimilarities evidently have yet to be reported for aqueous solutions of the diastereoisomers of other compounds. Ward, Pettijohn, Lockwood, and Coghill (11) and Knowlton, Schieltz, and Macmillan (4) have attributed these well established differences between the 2,3-butanediols to hydrate formation by the *meso-* and lack of hydrate formation by the *levo-*isomer. The ability of the *meso-*form to yield a hydrate that crystallizes above the freezing point of water provides conclusive evidence for hydration in its aqueous solutions. The *levo-*isomer possesses the same functional groupings, however, and there is no immediately apparent reason for supposing that it differs greatly from the *meso-*isomer in its affinity for water. Apart from its failure to yield an isolable hydrate, the existing experimental evidence on the *levo-*isomer indicates that its aqueous solutions are characterized by hydration. This isomer is strongly hygroscopic and exhibits considerable heat of solution on mixing with water. The density of its aqueous solutions exceeds those of

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either pure component over a wide range of concentrations (7). Freezing point lowering by the *levo*-isomer consistently exceeds the values calculated from the Raoult–van't Hoff equation. Aqueous solutions of the *levo*- and *meso*-isomers also exhibit a striking similarity in their absolute viscosity/diol concentration relations (2). If hydration occurs in aqueous solutions of either isomer, their differences in freezing point require reinterpretation.

Ward *et al.* (11) and Neish (6) reported specific rotation values above −13° for pure *levo*-2,3-butanediol. From the results of an intensive study, Neish (6) concluded that the 2,3-butanediol formed in the *Aerobacillus polymyxa* fermentation consists entirely of the *levo*-isomer. Butanediol samples obtained with *Aerobacillus* often show low polarization values (2, 4). Knowlton *et al.* (4) claimed that such samples were contaminated with the *meso*-isomer, presumably formed in the fermentation. To clarify this point, information appeared desirable on the effects of temperature and of traces of water and esterified butanediol on the "specific" rotation value.

When plotted against diol concentration, existing data on the refractivity of aqueous *levo*- and *meso*-2,3-butanediol solutions show serious irregularities (4, 8). The magnitude of the effects of temperature on this property also had not been established.

The situation as outlined above prompted the present study, which is concerned chiefly with the effects of diol concentration and temperature on the specific gravity, optical rotatory power, and refractivity of aqueous 2,3-butanediol solutions.

Materials and Methods

The 2,3-butanediols were prepared from fermented wheat mashes by methods that have already been described in detail (6, 10) and were redistilled at 40 to 45 mm. of mercury immediately before use. The diol obtained with *Aerobacter aerogenes* ($[\alpha]_D^{20} = +0.8°$) will be referred to as the *meso*-isomer, it being understood that the usual 5 to 10% of *dextro*-isomer was present. Solutions were prepared by accurate weighing, and, unless otherwise stated, the data are expressed on a weight percentage basis.

The diacetate of the *levo*-isomer was prepared by mixing 117 gm. acetic anhydride, 45 gm. *levo*-2,3-butanediol, and one drop of concentrated sulphuric acid, and allowing to stand one day at room temperature. The solution was distilled at 5 to 10 mm. of mercury, and the fraction boiling at 76 to 78° C. was collected. The crude diacetate was purified by crystallization from petroleum ether, yield 45 gm.

Specific gravity was determined by the conventional pycnometer method with minor modifications (3), temperature control being within ± 0.02° C. Before beginning the present series of estimations, reproducibility of the technique was tested against distilled water. Ten successive specific gravity measurements agreed to the nearest fifth decimal point, the standard deviation for the weight of the filled pycnometer being ± 0.0005 gm. Since other sources of error could not be entirely excluded, the data for diol solutions were calculated to the nearest fourth decimal point. Corrections were not introduced for air buoyancy because of their uniformly low magnitude.

Isothermal contraction in volume on mixing 2,3-butanediol with water was determined by calculating the volume of the components before and after mixing at each temperature, expressing contraction as millilitres per 100 ml. initial volume (1, p. 57). Thermal expansion was determined from the equation $d_4^{20}/d_4^{40} = 1 + 20\,\alpha$, which is an adaptation of the expression $V_t = V_o\,(1 + \alpha\, t)$.

The refractive index values were obtained with a Bausch and Lomb Abbé refractometer. The polarimetric measurements were made with an Adam Hilger polarimeter, and a General Electric sodium vapour lamp was employed as light source. The liquids were brought to bath temperature before they were placed in water-jacketed polarimeter tubes. During the course of the refraction and optical rotatory power measurements, temperature control was maintained within ± 0.1° C.

Results

Specific Gravity

With increasing diol content, the specific gravity of aqueous 2,3-butanediol solutions rises to a maximum at 50 to 60% diol, and then declines gradually to the values of the anhydrous isomers (Figs. 1, 2). The similarity of the

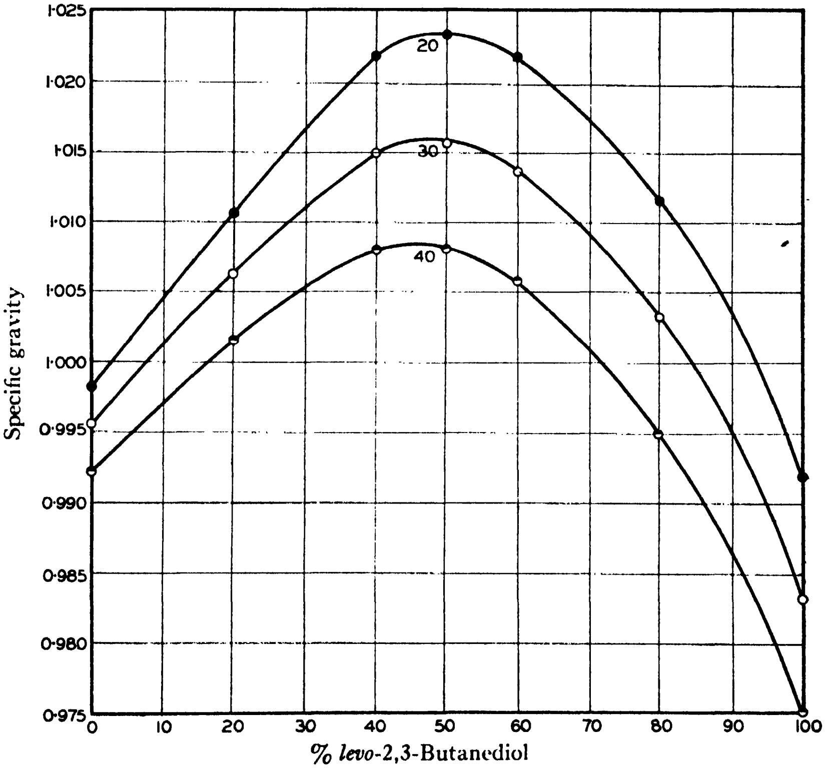

FIG. 1. *Specific gravity of aqueous levo-2,3-butanediol solutions at 20°, 30°, and 40° C.*

changes in specific gravity resulting from the effects of concentration and temperature indicates that the affinities of the *levo-* and *meso-*isomers for water are approximately equivalent.

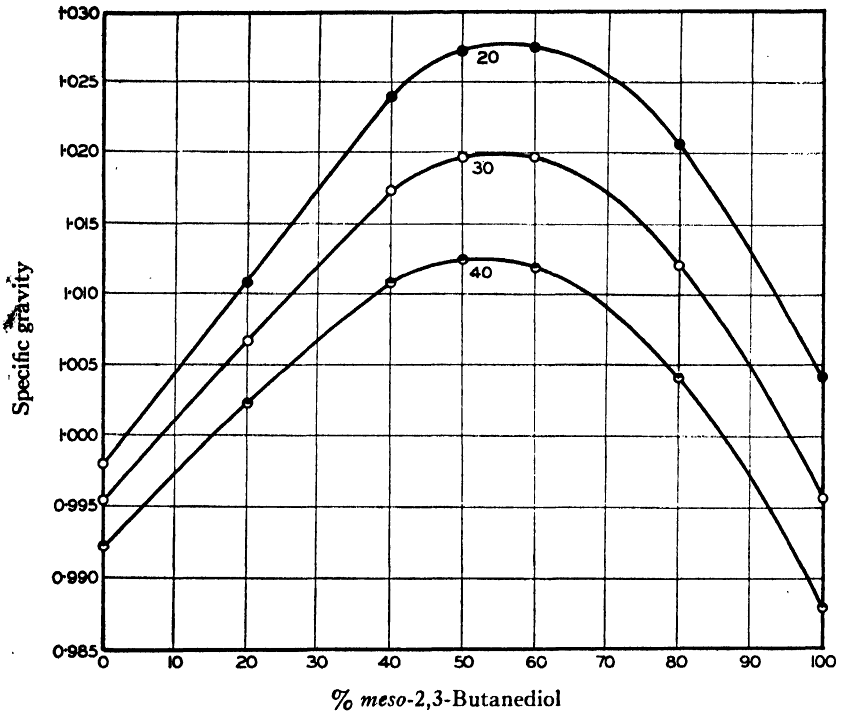

FIG. 2. *Specific gravity of aqueous meso-2,3-butanediol solutions at 20°, 30°, and 40° C.*

Contraction on Mixing

Tables I and II provide derived data on the contraction in volume that occurs on mixing 2,3-butanediol isomers with water in different proportions at 20°, 30°, and 40° C. Slightly less contraction occurs on mixing water with the *meso-* as compared with the *levo-*isomer. The cause of this difference

TABLE I

CONTRACTION IN VOLUME ON MIXING *levo*-2,3-BUTANEDIOL WITH WATER AT DIFFERENT TEMPERATURES

Wt. of glycol, gm.	Wt. of water, gm.	Contraction in ml. per 100 ml. initial volume		
		20° C.	30° C.	40° C.
9.9990	40.1195	1.35	1.27	1.26
20.0014	30.0580	2.59	2.38	2.26
25.0153	25.1259	2.66	2.57	2.43
30.0467	20.1089	2.70	2.50	2.37
40.0060	10.0074	1.83	1.72	1.66

TABLE II

CONTRACTION IN VOLUME ON MIXING *meso*-2,3-BUTANEDIOL WITH WATER AT DIFFERENT TEMPERATURES

Wt. of glycol, gm.	Wt. of water, gm.	Contraction in ml. per 100 ml. initial volume		
		20° C.	30° C.	40° C.
10.0141	40.0192	1.14	1.10	1.10
19.9990	30.2180	2.28	2.11	2.02
25.0276	25.0238	2.51	2.31	2.18
30.0111	20.2621	2.49	2.31	2.21
40.0242	10.0277	1.74	1.60	1.52

evidently lies in the more compact structure or closer association of the *meso*-isomer in the anhydrous state. Less contraction occurs on mixing butanediol and water at high than at low temperatures, temperature having greatest effect at diol concentrations of 40 to 60%. Within the investigated temperature range, maximum contraction was consistently observed at butanediol concentrations of 50 to 60%.

Thermal Expansion

The coefficient of thermal expansion for 2,3-butanediol solutions increases as the water content is reduced (Table III). With rising temperature the *meso*-form undergoes slightly less expansion than the *levo*-form, both in the presence and absence of water. Since molecular movement in the aqueous solutions is impeded to a slightly greater extent by the *meso*- as opposed to the *levo*-configuration it would appear that small but real differences exist between the isomers in their degree of affinity for water.

TABLE III

THERMAL EXPANSION OF AQUEOUS 2,3-BUTANEDIOL SOLUTIONS BETWEEN 20° AND 40° C.

Diol, %	$\alpha \times 10^3$*	
	levo	*meso*
0	0.30	0.30
20	0.45	0.42
40	0.77	0.65
50	0.75	0.72
60	0.79	0.76
80	0.83	0.81
100	0.85	0.82

* *Calculated from the equation* $d_4^{20}/d_4^{40} = 1 + 20\alpha$

Optical Rotatory Power

The polarization value of optically active 2,3-butanediol isomers is the most commonly used criterion of their relative purity. On the assumption that impurities reduce the specific rotation, the purest sample should have the highest specific rotation value. The highest value for the *levo*-isomer ($[\alpha]_D^{26}$ = −13.34°) was reported by Neish (6) and the corresponding 1 dm. polarization value, uncorrected for density, was −13.19°.

Samples of *levo*-2,3-butanediol often show polarization values considerably less than −13° although their boiling points, refractive indices, and densities closely approximate those of samples having polarization values above −13°. Since acetic acid is produced in considerable quantities in the *Aerobacillus polymyxa* fermentation, the mono- and diacetates are apt to be present as impurities in the recovered diol. The diacetate of the *levo*-form showed the following properties: n_D^{25} 1.4132; d_4^{20} 1.029; $[\alpha]_D^{28}$ + 13.65°. The presence of this compound as an impurity would accordingly have considerable effect on the polarization value although causing little change in the refractive index

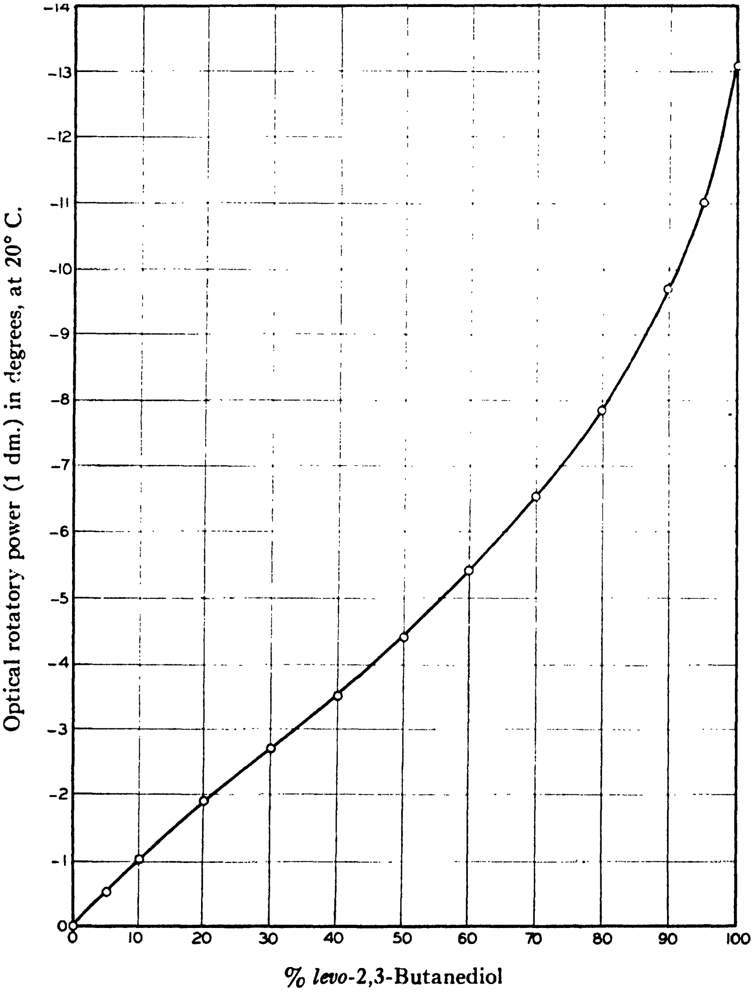

FIG. 3. *Optical rotatory power of aqueous levo-2,3-butanediol solutions at 20° C.*

and density. The same is believed to apply to the monoacetate, although its effect on the polarization value undoubtedly would be less pronounced.

Since 2,3-butanediols are strongly hygroscopic, the effect of water on the rotatory power of the *levo*-isomer warrants consideration as a possible cause of low polarization values. Fig. 3 shows that the polarization value is reduced very markedly by small amounts of water, the solvent influence being considerably greater than if water were merely serving as an inert diluent. Such an effect suggests polar association of water and *levo*-2,3-butanediol as the most probable cause. Since rising temperature leads to dissociation of higher order compounds, the effects of water on the optical rotatory power of *levo*-2,3-butanediol should be strongly influenced by changes in temperature, high temperatures leading to diminished hydration and consequent reduction of the effects of water on the polarization value.

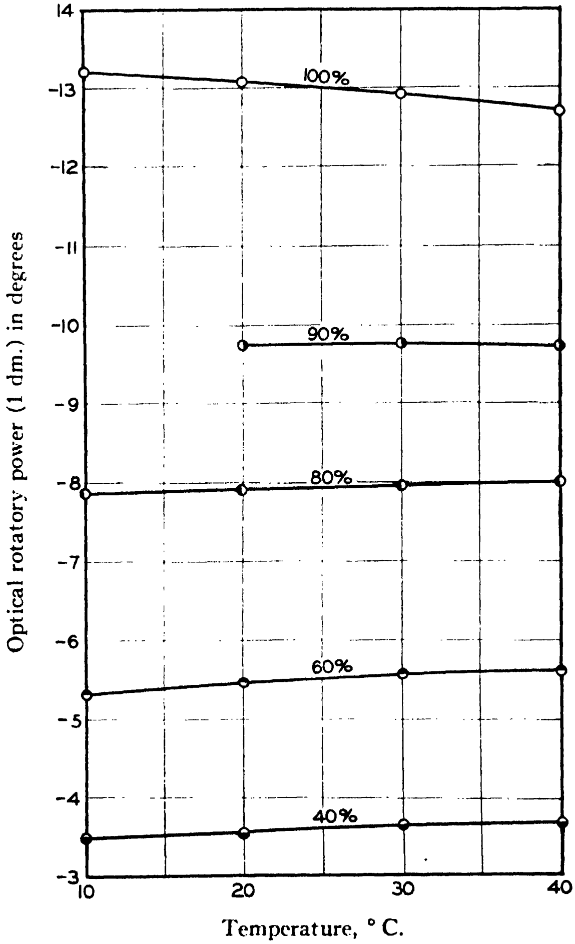

FIG. 4. *Influence of temperature on the optical rotatory power of levo-2,3-butanediol and of its aqueous solutions at concentrations of 40 to 90%.*

Fig. 4 shows that the optical rotatory power of anhydrous *levo*-2,3-butanediol is reduced by rising temperature. In the presence of 20% or more of water, the dominant effect of rising temperature on the polarization value arises from hydrate dissociation; in the presence of 10% of water, the opposing effects of temperature are almost exactly balanced. As might be anticipated from the specific gravity data, the 60% solution shows a larger increase in polarization value with rising temperature than either the 80 or 40% solutions.

In Fig. 5, the optical rotation data are presented as specific rotation, calculated from the conventional formula $[\alpha] = \frac{\alpha}{l \epsilon \delta}$, where α = observed rotation in degrees, l = length of column in decimetres, δ = density of the liquid, ϵ = fraction by weight of the optically active compound. At 20° C.

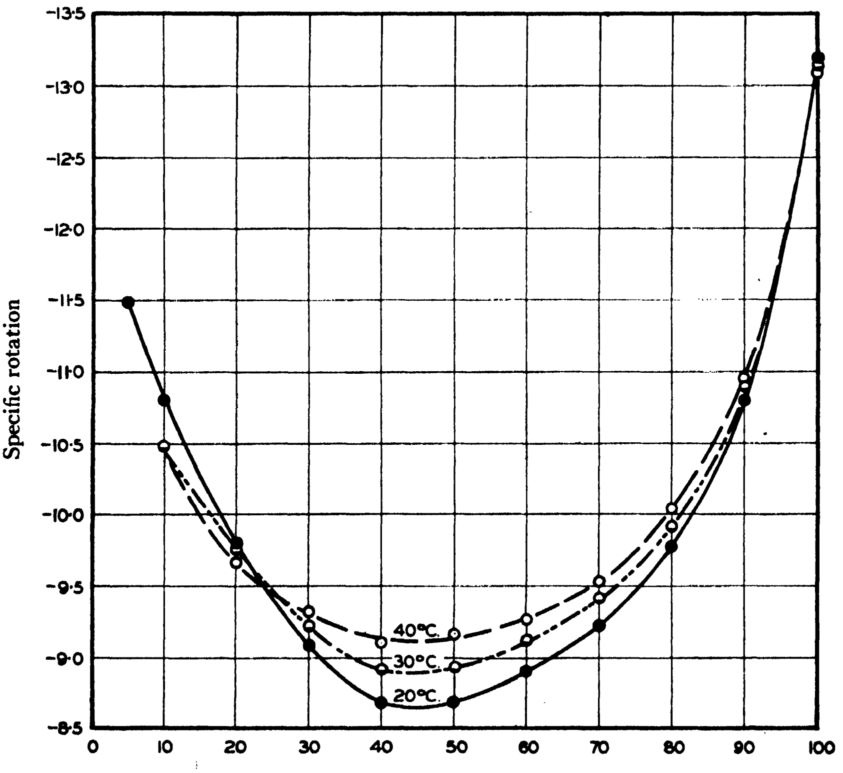

FIG. 5. *Effects of concentration and temperature on the specific rotatory power of levo-2,3-butanediol in aqueous solution.*

the specific rotation value is reduced from −13° for the anhydrous liquid to approximately −9° for solutions containing 30 to 60% diol. With diol concentrations of 30 to 90%, the specific rotation values are consistently higher at 30° and 40° C. than at 20° C. On dilution to concentrations of 20% diol and less, the specific rotation value rises. Evidently as the butanediol molecules become widely separated, association of water with water becomes increasingly important, with consequent reduction in the effect of the solvent on the optically active solute.

Refractive Index

The refractive indices of aqueous solutions of the *levo-* and *meso-*isomers of 2,3-butanediol presented in Fig. 6 show general conformity with the data presented by Othmer, Shlechter, and Koszalka (8) and Knowlton, Schieltz, and Macmillan (4) respectively. The molar refractivity, calculated from the expression $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d}$, is 23.59 for the *meso-* (n_D^{25} 1.4366, d_4^{25} 0.9998) and 23.62 for the *levo-*isomer (n_D^{25} 1.4308, d_4^{25} 0.9873). The value calculated from tables of refraction equivalents is 23·56 (6).

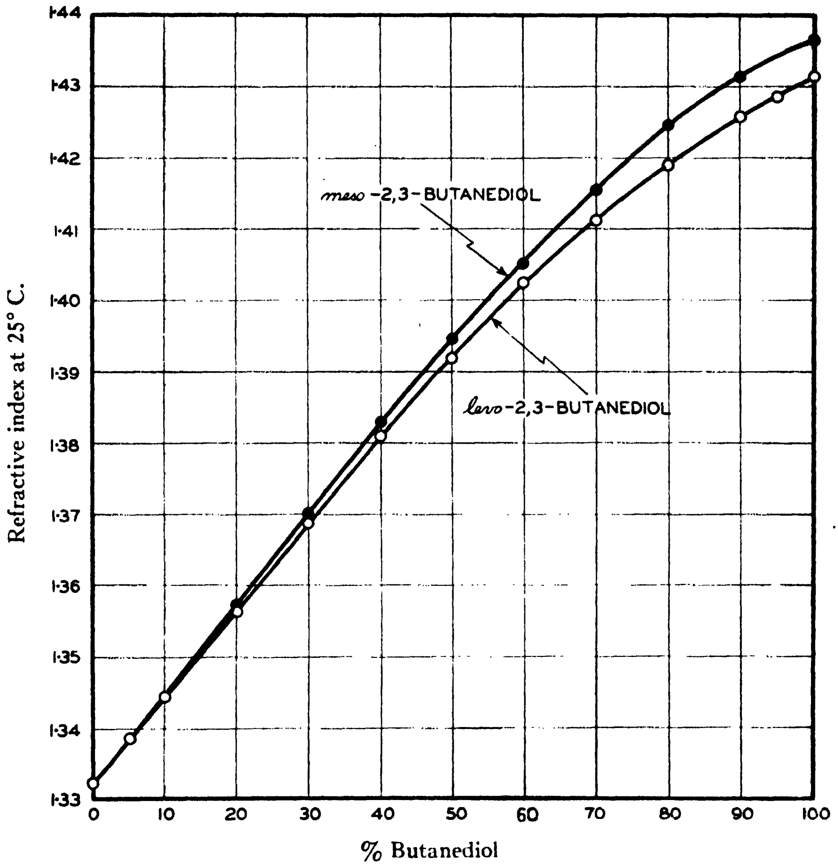

FIG. 6. *Refractive indices of aqueous solutions of meso- and levo-2,3-butanediol at 25° C.*

The data of Table IV, which were obtained with a relatively impure sample of *levo-*2,3-butanediol ($[\alpha]_D^{20} = -12.92$), are included for purposes of reference in practical control work. Sensitivity of the refractive index values to

TABLE IV

REFRACTIVE INDICES OF AQUEOUS *levo*-2,3-BUTANEDIOL SOLUTIONS AT DIFFERENT TEMPERATURES

Diol, %	Temp., ° C.			
	20	25	30	35
0	1.3330	1.3325	1.3319	1.3312
10.0	1.3450	1.3445	1.3437	1.3429
19.9	1.3574	1.3566	1.3557	1.3549
29.9	1.3700	1.3689	1.3677	1.3666
39.9	1.3820	1.3807	1.3793	1.3779
49.9	1.3930	1.3915	1.3900	1.3885
59.6	1.4027	1.4012	1.3997	1.3982
70.0	1.4115	1.4098	1.4082	1.4065
79.7	1.4197	1.4180	1.4162	1.4146
89.7	1.4264	1.4247	1.4229	1.4212
99.5	1.4322	1.4302	1.4283	1.4264

temperature change is strongly influenced by diol concentration. The data of Table IV indicate that the refractive index values are not changed sufficiently by 0.5° variation in temperature to exceed the error of observation (± 0.0003) with the Abbé refractometer.

Discussion

The specific gravity and specific rotation data presented above are considered to establish the importance of hydration in aqueous solutions of *levo*- as well as *meso*-2,3-butanediol. In seeking an alternative explanation to that offered by Ward *et al.* (11) for the marked differences in their freezing points, attention should be drawn to the basic distinction between crystalline and amorphous states: crystals are characterized by oriented lattice structures, amorphous states by random arrangement. In the absence of water, the *meso*-isomer freezes or forms oriented lattice structures at a higher temperature than the *levo*-isomer. Both isomers undergo hydration in aqueous solution, and the configurational influence is again responsible for the decidedly greater difference in freezing point that is exhibited in this state: upon hydration, the difference in orientation tendency shown by the anhydrous isomers is greatly magnified.

The present demonstration of the effect of water on the specific rotatory power of *levo*-2,3-butanediol represents additional information on a relatively obscure aspect of solvent action. Landolt (5) reported that water had a remarkable and puzzling influence on the specific rotation values of ethyl tartrate and nicotine: on diluting ethyl tartrate with water to a concentration of 10%, the specific rotation value rose progressively from + 8.5° to +26.2°; similar treatment of nicotine reduced its specific rotation from −162° to −76°. Patterson (9) showed that the solvent effect observed with ethyl tartrate was progressively reduced on replacing water with methanol, ethanol, and pro-

NOTICE

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panol, respectively. A similar reduction of the solvent effect was observed by Winther (12, 13) in corresponding studies of nicotine solutions. Solvents representing a graded polarity series, such as were used by these investigators, presumably would cause a similar modification of the specific rotation value of *levo*-2,3-butanediol. Since its molecules are of simple structure and have polar substituents on the asymmetric carbon atoms, *levo*-2,3-butanediol should be particularly useful in further studies of solvent influences.

Acknowledgments

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THE DETECTION OF ETHYL*BIS*(β-CHLOROETHYL)AMINE[1]

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Abstract

Aqueous solutions of ethyl*bis*(β-chloroethyl)amine and Reinecke salt react to yield a pink crystalline precipitate. The sensitivity of the test depends on a number of factors, but, under suitable conditions, Reinecke salt will detect less than 5 p.p.m. of this amine in aqueous solution.

Introduction

Ethyl*bis*(β-chloroethyl)amine, $C_2H_5N(CH_2CH_2Cl)_2$, is closely related structurally to substances that have an irritating (trichlorotriethylamine (16)) or vesicant (methyl*bis*(β-chloroethyl)amine (9)) action on the skin.* It does not appear to have been noted that Reinecke salt (5, pp. 555-556), $NH_4[Cr(NH_3)_2(SCN)_4] \cdot H_2O$, may be used for the detection of ethyl*bis*(β-chloroethyl)amine or water contaminated with this amine. It is well known, however, that Reinecke salt or the corresponding acid serves as a precipitant for many organic bases (1, 2, 3, 10, 20) and for a number of amino acids (4, 7, 15, 19). Reineckates may be used to aid in the characterization of certain bases (8, 17), and are of service in effecting a number of isolations and separations (11, 12, 13, 14, 19, 20, 21). It was in the form of reineckates, for example, that the antibiotically active bases streptomycin and streptothricin were first obtained in the form of crystalline salts (6).

Experimental

It was found that when ethyl*bis*(β-chloroethyl)amine is added to an aqueous solution of Reinecke salt, a precipitate is formed (unless the concentrations of reactants are too low).

Nature of Precipitate

The precipitate is composed of tiny pink lustrous crystals. An attempt was made to determine the melting point of the crystals, but it was found that they

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* *Since this paper was written, the pathologic effects of ethylbis(β-chloroethyl)amine (a vesicant of the "nitrogen mustard" family) have been published (Graef, et al., Federation Proc., Part II, Vol. 5, pp. 221-2, Feb. 1946). Attention was drawn to the peace-time biochemical and medical interest in the nitrogen mustards at the meetings of the Federation of American Societies for Experimental Biology and of the American Association for Cancer Research, held in Atlantic City, N.J., in March, 1946, and at the 109th meeting of the American Chemical Society held at Atlantic City, N.J., in April, 1946. The biological actions of nitrogen mustards and their possible therapeutic applications in the treatment of Hodgkin's and other diseases have recently been discussed by Gilman and Philips (Science, 103 : 409-415. (April 5, 1946)).*

PLATE I

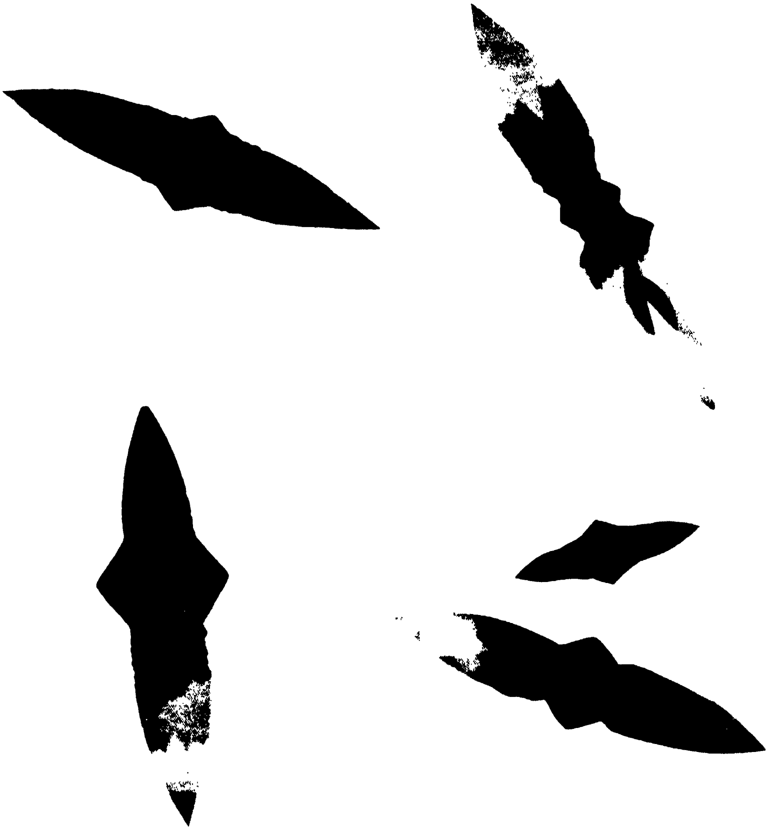

FIG. 1. *Electron microscope pictures of reineckate crystals (obtained through the courtesy of the Radiology Section of the National Research Council of Canada). Magnification: 400-600.*

decomposed on heating; darkening and shrinking of the crystals was observed at 132° C. (corr.) (the dark red-brown decomposition product melted below 187° C.).

Photographic studies have indicated that the shape of the crystals depends to some extent on the conditions of precipitation, viz., age of reactant solutions, and absolute and relative concentrations of amine and Reinecke salt, but in all cases the crystals are definitely elongated. With a given set of conditions, more than one type of crystal may be obtained; in Fig. 1 are shown several shapes of crystals formed by the interaction of one-day-old solutions of amine and Reinecke salt. Under other conditions, elongated crystals with distinctly serrate edges may be obtained.

Relation of Precipitation to Age of Amine Solution

A number of experiments were carried out in which the amount of reineckate precipitate was studied as a function of the age of an aqueous solution of the amine. The precipitations were carried out in a graduated conical centrifuge tube in which the volume of precipitate was read after centrifugation. The volume of precipitate so obtained depends not only on the age of the amine solution and on the time and the rate of centrifugation, but also on the time allowed for interaction before centrifugation and on the age of the Reinecke salt solution (Reinecke salt is not stable in aqueous solution (5, pp. 555-556)). With the adoption of a fixed technique of experimentation, it was found possible to obtain good checks in following the variation in the amount of precipitate produced as the amine solution aged (at room temperature). Fig. 2 shows a plot of the results obtained over a 25 hr. period (1% aqueous

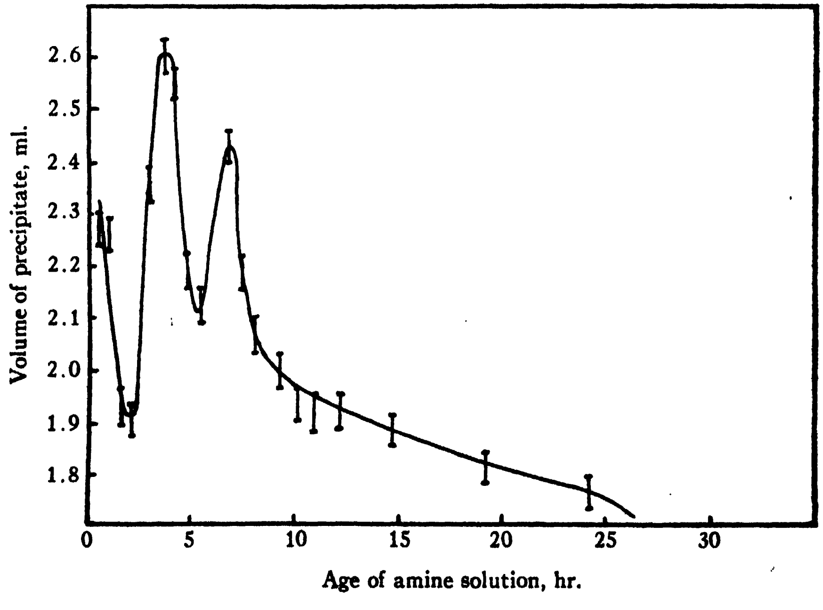

FIG. 2. *Variation in reineckate precipitation with age of amine solution.*

solutions of the amine and Reinecke salt were mixed so that the resultant concentrations, before interaction, were 2.00×10^{-2} ml. of amine and and 8.00×10^{-2} gm. of salt in 10.00 ml. of solution).

In other similar experiments, which were carried out under slightly different conditions, the presence of maxima in the curve during the first 11 hr. in the life of the amine solution was confirmed, although the position of the maxima relative to the time scale was observed to depend, like the volume of precipitate recorded, on the details of the experimental technique. As the amine solution ages beyond 25 hr. the yield of reineckate precipitate decreases, but at a decreasing rate; tests were carried out over a period of 1350 hr., but the amount of precipitate was essentially constant (0.4 ml.) after about 600 hr.

It may be mentioned that in these and other experiments, it was found that an apparatus similar to the one described by Schneider (18) was very useful for filling and delivering the micropipette employed for measuring the liquid amine.

Use of Reinecke Salt for Detection of Amine

The sensitivity of this test for the detection of ethyl*bis*(β-chloroethyl)-amine in aqueous solution was determined, using aqueous amine solutions of various concentrations, by noting the lowest concentration of amine that would yield a detectable amount of reineckate precipitate under fixed conditions of experimentation. The procedure employed was as follows.

From a microburette, 2.00 ml. of dilute amine solution was run into a 15 ml. conical graduated (to 0.1 ml.) centrifuge tube and 8.00 ml. of 1% aqueous Reinecke salt solution (centrifuged or filtered free of any sediment just prior to use) rapidly added; the resultant solution was allowed to stand for one minute during which time it was stirred, and then it was centrifuged under reproducible conditions. All determinations were carried out in duplicate; good checks were obtained. The "limit of detection" in Table I refers to the concentration of amine in solution before the fivefold dilution with Reinecke salt solution.

TABLE I

SENSITIVITY OF REINECKATE TEST

Reinecke solution	Amine solution	Limit of detection
Freshly prepared	Aged* 10 days	Between 5 and 10 p.p.m.
Aged* 25 hr.	Aged* 10 days	Between 1 and 5 p.p.m.
Aged* 27 hr.	Freshly prepared	Between 1 and 5 p.p.m.

* *At room temperature.*

The test is appreciably less sensitive if one depends on visual detection of the amine reineckate precipitate previous to centrifugation. The very tiny lustrous crystals formed on the addition of the Reinecke salt solution to a freshly prepared (or one-day-old) solution of the amine containing the latter at a concentration of one part in 20,000 are, however, evident without centrifugation within a minute after the solutions are mixed.

Other Possible Precipitants for Amine

Aqueous solutions of a number of complex chromium compounds related to Reinecke salt, viz., $(NH_4)_3[Cr(SCN)_6]$, $K_3[Cr(SCN)_6]$, $Cr(NH_3)_3(SCN)_3$, $[Cr(NH_3)_4(SCN)_2]$ (SCN), and $[Cr(NH_3)_5(SCN)]$ $(SCN)_2$, were tested for their reactivity toward ethyl*bis*(β-chloroethyl)amine. On the addition of liquid amine to solutions of these compounds it was found that, although in most cases spectrophotometric examination of the solutions gave some evidence of reaction, distinct precipitates were produced only with the two hexathiocyanato compounds. These precipitates were light blue in colour, and not nearly as voluminous as the precipitate produced by Reinecke salt under the same conditions of experimentation. The same two chromiates will also react, at suitable concentrations, with aged aqueous solutions of the amine to yield precipitates similar or identical to those produced by dissolving liquid amine in solutions of the complex compounds. Ammonium and potassium hexathiocyanato chromiates are much inferior to Reinecke salt for the purpose of detecting the amine; sensitivity tests of the type described above (but using 12-day-old amine) showed the limit of detection to be between 0.1 and 1%.

Discussion

The experiments in which photographs (Fig. 1) were taken indicate that it is probable that the hydrolysis of ethyl*bis*(β-chloroethyl)amine gives rise to several products, more than one of which react with an aqueous solution of Reinecke salt. The experiments with an ageing solution of the amine furnish further evidence that the mechanism of the hydrolysis of this amine is a complicated one, and make it evident that Reinecke salt cannot be conveniently employed for the quantitative estimation of ethyl*bis*(β-chloroethyl)-amine when the latter is in fresh aqueous solution.

The reaction of a solution of Reinecke salt with the amine forms the basis of a qualitative test for the detection of the latter—a test that will detect, under controlled experimental conditions, less than 5 p.p.m. of the amine in aqueous solution. Reinecke salt is more suitable for this test than a number of complex chromium compounds structurally related to it.

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LIQUID-VAPOUR EQUILIBRIUM FOR THE SYSTEM HYDROGEN-CYANIDE–CYANOGEN-CHLORIDE[1]

By A. R. Gordon[2] and G. C. Benson[3]

Abstract

The binary liquid–vapour equilibrium for the system hydrogen-cyanide–cyanogen-chloride has been investigated at 15° C. The equilibrium liquid–vapour compositions were determined by slow isothermal distillation and the vapour pressures by mercury manometer. Analysis of the phases was by density, independent measurements having fixed the density–liquid composition curve. It is shown how true equilibrium compositions may be obtained from the measured (average) compositions of the distillates.

The measurements reported here were undertaken to study the vapour-liquid equilibrium for the system hydrogen-cyanide–cyanogen-chloride. The results, although not susceptible of analysis by means of the Gibbs–Duhem equation as were those for the systems ethanol–acetone (4) and ethanol–ethyl-ether (5), are nevertheless of interest. Moreover, the technique employed—slow isothermal distillation—is so simple, and of such wide applicability that we believe attention should be called to it, especially since certain corrections may now be made that largely remove the difficulty of interpreting conventional distillation data in terms of equilibrium concentrations.

Experimental

The apparatus is illustrated in Fig. 1, and somewhat resembles that of Roberts and Mayer (9); the principal differences are that Roberts and Mayer used mercury U's in place of stopcocks, and that their distillations involved the removal of only about 1% of the liquid phase as compared with the 5 to

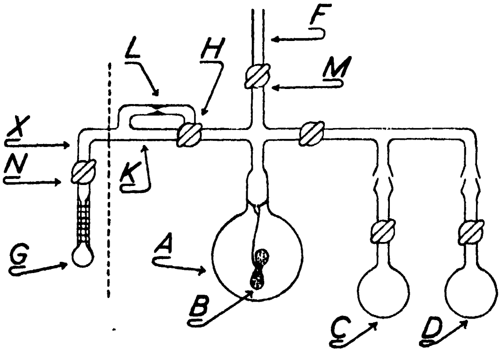

Fig. 1.

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7% used in this research; the practical advantage of being able to use a larger distillate fraction is obvious. The small flask *A* of approximately 40 cc. capacity contains the liquid phase; suspended by platinum in its neck, is the small glass bulb *B*, containing iron filings, which can be made to oscillate and thus stir the liquid by means of a solenoid controlled through a commutator. *C* and *D* are glass bulbs containing the purified hydrogen cyanide and cyanogen chloride; they are provided with pressure stopcocks and standard taper joints for attachment to the filling manifold. The lead to the vacuum pump, McLeod gauge, and mercury manometer is shown at *F*; the manometer level was read on an etched glass scale ruled on the dividing engine in the Physics Department of this University, and checked by microscope comparator. The distillate receiver is the pycnometer bulb *G* of approximately 1 ml. capacity; a scale is etched on the capillary neck, and the volumes corresponding to the various scale divisions were determined by weight calibration with mercury according to the procedure of MacInnes, Cowperthwaite, and Huang (7). *A* and *G* are connected by the three-way stopcock *H*, either through the tube *K* of 5 mm. internal diameter, or through the tube *L*, which has a constriction in it 0.1 mm. in diameter.

In carrying out a measurement, roughly estimated amounts of the components in the flasks *C* and *D* were repeatedly outgassed by first freezing with liquid air, pumping off the residual gas, and then melting; this was continued until the residual air pressure after freezing was less than one micron as measured on the McLeod gauge. It is essential to remove air as completely as possible from the system since otherwise air will accumulate in *G* as the distillation proceeds, and the transport process through the capillary will be diffusion controlled. After outgassing, the flasks were removed from the manifold, allowed to come to temperature equilibrium, and weighed; blank experiments showed that loss in weight during the process of weighing was undetectable. The flasks were again attached to the manifold, the apparatus was evacuated (with tap *H* turned to tube *K*) and the contents of *C* and *D* were distilled into *A* with liquid air; as a rule the total charge thus introduced was from 15 to 25 gm. *C* and *D* were finally weighed empty, thus fixing the composition of the system gravimetrically.

The contents of *A* was once again thoroughly outgassed as described above; blank experiments in which the frozen sample was exposed to the Hyvac pump for one hour showed that the total loss in weight over this period was only 0.2 mgm. With stopcock *H* closed, the water-bath, which contained the whole apparatus to the right of the broken line in the figure, was filled and brought on temperature, stirrer *B* was started, and the vapour pressure of the liquid in *A* was read; the bath temperature was fixed by standard thermometers calibrated against the platinum resistance thermometer, which is temperature standard for this laboratory (4).

After reading the vapour pressure, the vapour in the lines was condensed back into *A* with liquid air, tap *M* was closed, the bath again brought on temperature, the stirrer started, and, when temperature equilibrium had been reached, *A* was connected to *G* through *L*. Since *G* was outside the main thermostat in a small bath whose temperature was manually controlled, it was possible to carry on the distillation as slowly as desired; as a rule, the temperature of the small bath was initially about 3° C. below that of the main bath, but as the distillation proceeded it was found necessary to increase the temperature difference somewhat in order to maintain a roughly uniform rate of distillation. Normally the distillation of the 1 ml. of liquid which constituted the distillate required from one to one and a half hours, although in some runs the time was as great as three hours; in no case was there any evidence that the results depended on the rate of distillation, thus indicating that the conditions were not significantly different from those obtaining at equilibrium. When sufficient distillate had collected to fill *G* almost to the neck, tap *H* was closed, the vapour to the left of *H* was condensed into *G* with liquid air, tap *N* was closed, and *G* was detached from the apparatus with a blow torch at *X*, the resulting glass tip being broken off. The contents of *G* was just melted and vigorously shaken, and *G* was then placed in a glass sided water-bath whose temperature was maintained at 15° C. Owing to the expansion on warming, the level of the liquid rose into the capillary neck, where the exact level of the meniscus in relation to the etched scale could be read on the graticule in a telescope; since one scale division corresponded to approximately 0.005 ml., and since the level of the meniscus could easily be read to one-fiftieth of a scale division. the volume of the distillate could be determined with a precision of 0.01%. It should be added that once temperature equilibrium had been established in the bath, there was never any creep in the position of the meniscus, thus showing that the liquid in *G* was of uniform composition. The pycnometer was then removed from the bath, dried and weighed; tap *N* was opened, and the contents was allowed to evaporate in a fume hood. A final weighing then fixed the weight and consequently the density of the distillate. As a final check, the entire contents of the apparatus to the right of tap *H* was condensed at the end of the run into a small flask (not shown in the diagram) and weighed; as a rule, the weight so found plus that of the distillate agreed with the sum of the weights of the components initially introduced within 1 mgm.

The density–liquid-composition curve for the system was determined by distilling into mercury-calibrated pycnometer bulbs of approximately 1 ml. capacity first hydrogen cyanide and then cyanogen chloride, the weights distilled being determined by the loss in weight of small filling tubes as described above. Here the sum of the weights distilled agreed with the measured weight of the contents of the pycnometer within 0.02% or better.

The liquefied gases were supplied by the National Research Council. The hydrogen cyanide was fractionally distilled through phosphorus pentoxide five or six times, the first and last fractions being rejected each time. The vapour pressure of the purified material at 15° C. was 501.8 mm., which is moderate agreement with the value predicted by Giauque and Ruehrwein's vapour pressure equation, viz., 502.6 mm. (2). The equation previously deduced by one of us (3) to represent Perry and Porter's vapour pressures (8) gives 503.2 mm. The cyanogen chloride was first distilled through phosphorus pentoxide and then fractionally crystallized repeatedly until its setting point became constant at −6.90 ± 0.02° C. in agreement with the findings of Winkler (12). Its vapour pressure at 15° C. was 833.0 mm. A plot of the vapour pressures reported by Klemenc and Wagner (6) indicates that this value is from 5 to 10 mm. above their curve; there is so much variation between their individual results, however, that any precise comparison is impossible. Whether the large discrepancy is due to difference in technique or is caused by different purity in the materials used is difficult to decide. It should be mentioned that different preparations of purified cyanogen chloride differed in their vapour pressures by not more than one- or two-tenth's of a millimetre; our value quoted above is an average.

Before the measurements discussed above can be interpreted, it is necessary to take account of the fact that in all the density measurements there was vapour above the liquid phase of slight but appreciable weight and of composition different from that of the liquid; the same is true for the vapour pressure determinations and for the calculation of the final composition of the liquid in bulb *A*; see reference (4). Accordingly, provisional density–liquid-composition, vapour-composition–liquid-composition, and vapour-pressure–liquid-composition curves were drawn ignoring this correction; the resulting correction both in weight and composition of the liquid concerned was then computed on the assumption that the vapour density of the vapour above a given liquid could be calculated by the gas laws from the provisional curves. The assumption of ideality is certainly untrue for hydrogen cyanide (see below) and is probably untrue for cyanogen chloride as well. However, owing to the relatively small vapour volumes involved (of the order of 0.4 cc. in the pycnometer measurements and of 40 cc. in the vapour pressure measurements) the error resulting from this assumption is entirely negligible. Calculation showed that a second calculation, using the corrected curves of liquid density, vapour pressure, and vapour composition was unnecessary. Finally, all weights were corrected to vacuum and all pressures to millimetres of mercury at 0° C. and sea level.

There is however a correction of an entirely different nature which must be noted. In an experiment, the initial composition and amount of the liquid phase are known, but the distillate analysed is an average sample since the compositions of both liquid and distillate change during the distillation. Thus if the fraction of the original system distilled be x, and the initial and final mole fractions of the liquid be N_0 and N_F, the measured average composition of the distillate $\overline{Y}$ will be given by

$$x\overline{Y} = N_0 - (1 - x)N_F . \tag{1}$$

If Y stand for the true equilibrium vapour mole fraction corresponding to a liquid mole fraction N, then x, N_0, and N_F are connected by the well known relation

$$\ln (1 - x) = \int_{N_0}^{N_F} dN/(Y - N). \tag{2}$$

It is only when x is vanishingly small as in the measurements of Zawidzki (13) and of Roberts and Mayer (9) that the measured $\bar{Y}$ may be identified, as is often done, with either the true Y (N_0) or $Y(N_F)$. It is immediately evident that a somewhat better approximation will result from identifying $\bar{Y}$ with $Y(\bar{N})$, where $\bar{N}$ is defined by

$$(1 - x/2)\bar{N} = N_0 - x\bar{Y}/2 = (1 - x)N_F + x\bar{Y}/2. \tag{3}$$

$\bar{N}$ is thus the mean liquid composition if all the distillate had been of uniform composition $\bar{Y}$.

The question remains however as to the error introduced by this approximation. An estimate of this error, accurate enough except possibly in extreme cases, can be readily obtained from Equation (2) provided Y can be treated as sensibly linear in N over the range of x. In particular, if

$$Y = A + (B + 1)N. \tag{4}$$

Equation (2) can be integrated at once to give

$$A + BN_F = (A + BN_0)(1 - x)^B \tag{5}$$

Expansion of the right-hand side of (5) gives

$$N_F = N_0 - (A + BN_0)[x - (B - 1)x^2/2 + (B - 1)(B - 2)x^3/6..] \tag{6}$$

From (5) and (1) there results

$$\bar{Y} = A + (B + 1)N_0 - (A + BN_0)[(B + 1)x/2 - (B + 1)(B - 1)x^2/6..] \tag{7}$$

Combining (7) with (4) and (3) gives in turn

$$N(\bar{Y}) = N_0 - (A + BN_0)[x/2 - (B - 1)x^2/6 ..] \tag{8}$$

$$\bar{N} = N_0 - (A + BN_0)[x/2 - Bx^2/4 ..] \tag{9}$$

$$N(\bar{Y}) \approx \bar{N} - (A + BN_0)(B + 2)x^2/12 \tag{10}$$

$$\approx \bar{N} - (Y_0 - N_0)(dY/dN + 1)x^2/12. \tag{11}$$

In (11) $Y_0 - N_0$ and dY/dN may be replaced for purposes of approximation by $\bar{Y} - \bar{N}$ and $d\bar{Y}/d\bar{N}$; hence from a plot of $\bar{Y}$ versus $\bar{N}$ an estimate may be obtained at once of the correction which must be applied to Equation (3) to give the true equilibrium liquid composition corresponding to the measured (average) vapour composition. For most purposes this is all that is necessary, but in any event the resulting corrected $Y - N$ curve may be checked by tabular or graphical integration of Equation (2). In the experiments recorded here, x is at most 0.07, and since $\bar{Y} - \bar{N}$ and $d\bar{Y}/d\bar{N}$ are both relatively small, the second term in Equation (11) is at most 0.01 mole % and is consequently negligible.

Results

Table I gives the density results for the solutions; here *N* is the mole fraction of cyanogen chloride in the solution. A deviation plot from a quadratic in *N* gave densities for round values of the mole fraction, and from the resulting table, mole fractions could be obtained for experimentally determined values of *G* by interpolation using second differences. The vapour pressure measurements are summarized in Table II, and the equilibrium liquid–vapour compositions in Table III; in these *N* and *Y* refer to the liquid and vapour mole fractions of cyanogen chloride. For purposes of interpolation, deviation functions of the type discussed under Equation (1) of reference (5) were employed for the $Y - N$ data; the resulting deviation functions were at most 0.04 and consequently were suitable for graphical interpolation. In only four instances did the experimental points lie off the smooth curves as finally drawn by more than 0.05 mole % and in only two by more than 0.1 mole %, the discrepancy being approximately 0.2 mole % in both cases. The entries for round values of the liquid composition correspond to these deviation curves.

TABLE I

DENSITY OF CNCl–HCN SOLUTIONS AT 15° C. IN GM. PER ML.

x = weight fraction CNCl, N = mole fraction CNCl

x	0	0.1389	0.4082	0.4592	0.5258	0.6659
N	0	0.0662	0.2327	0.2718	0.3277	0.4670
G	0.6944	0.7380	0.8399	0.8622	0.8931	0.9658
x	0.7290	0.7957	0.8294	0.8746	0.9379	1.0000
N	0.5418	0.6313	0.6813	0.7541	0.8691	1.0000
G	1.0024	1.0440	1.0659	1.0967	1.1434	1.1920

TABLE II

VAPOUR PRESSURE OF CNCl–HCN SOLUTIONS AT 15° C.

N	0	0.0448	0.0777	0.1142	0.1261	0.1339	0.2483	0.2493
P, mm.	501.8	524.0	540.2	557.8	563.0	566.2	614.8	614.6
N	0.3293	0.4763	0.5586	0.7232	0.7793	0.8582	1.0000	
P, mm.	645.9	696.5	721.4	768.8	783.3	800.6	833.0	

TABLE III

VAPOUR–LIQUID EQUILIBRIUM FOR THE SYSTEM CNCl–HCN AT 15° C.

N	0.0761	0.1117	0.1317	0.2453	0.2459	0.3248
Y	0.1360	0.1926	0.2214	0.3677	0.3679	0.4535
N	0.4536	0.4727	0.5556	0.6293	0.7778	0.8571
Y	0.5801	0.5953	0.6633	0.7236	0.8347	0.8932

For the vapour pressures, a deviation plot of the type used by Scatchard and Raymond (10) was employed for values of N up to 0.5; for $N > 0.5$, the deviation from a linear function of N was plotted. In only four instances do the experimental points differ from the smooth curves drawn to represent the data by as much as 0.3 mm., and in the majority of cases by less than 0.2 mm. The entries in Table IV correspond to these curves.

TABLE IV

N	G	P, mm.	Y	N	G	P, mm.	Y
0	0.6944	501.8	0	0.40	0.9317	671.2	0.5295
0.025	0.7011	514.4	0.0470	0.50	0.9822	703.7	0.6195
0.05	0.7275	526.9	0.0920	0.60	1.0296	733.8	0.7005
0.10	0.7596	551.1	0.1750	0.70	1.0740	762.5	0.7775
0.15	0.7907	573.6	0.2470	0.80	1.1158	788.4	0.8510
0.20	0.8207	594.9	0.3125	0.90	1.1554	809.6	0.9250
0.30	0.8780	634.7	0.4290	1.00	1.1920	833.0	1.0000

A check on the self-consistency of our results by means of the Gibbs–Duhem equation is unfortunately not possible here owing to the uncertainty as to the equation of state for the vapour. Usherwood (11) and Felsing and Drake (1) have shown that hydrogen cyanide differs markedly from ideality through polymerization in the gaseous phase, and it would be surprising if cyanogen chloride did not show marked deviations as well. Nevertheless, the excellent reproducibility of the results indicates, we believe, that our measurements cannot be seriously in error.

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THE VAPOUR PRESSURE OF SOLUTIONS OF CARBON DIOXIDE IN DIFLUORODICHLOROMETHANE[1]

A. R. GORDON[2] AND E. A. MACWILLIAM[3]

Abstract

The vapour pressure of solutions of carbon dioxide in Freon has been determined at 10° and 20° C. for pressures up to 25 atm. At both temperatures, the vapour pressure is roughly linear in the mole fraction of carbon dioxide, the deviations being positive for solutions low in carbon dioxide and negative for solutions high in carbon dioxide; for a given concentration, the deviation becomes more negative the higher the temperature.

This research concerns the vapour pressure of the system carbon-dioxide–Freon (difluorodichloromethane) and was undertaken to provide data for possible uses of such chemically inert solutions.

Experimental

The experimental procedure consisted in condensing into a heavy glass bulb a sample of known composition and determining its vapour pressure by means of a closed-end mercury–air manometer. The apparatus is shown in Fig. 1. *A* is the bomb of Pyrex glass, capacity 12 cc. and wall thickness 3.5 mm.; it is contained in a water thermostat regulated to 0.005° C., bath temperatures being determined by means of a platinum resistance thermometer with National Bureau of Standards certificate. *A* is connected with the closed-end manometer *B*, which is contained in a glass-walled air thermostat regulated to 25.00 ± 0.05° C.; the height of the meniscus in *B* is read on a glass scale placed immediately behind the manometer. The dimensions of the manometer are such that at the highest pressures measured, viz., 25 atm., a movement of 0.05 mm. of the meniscus corresponds to a pressure change of 0.02 atm. The manometer was calibrated by determining the readings corresponding to the known vapour pressure of carefully dried ammonia, (5, p. 234) and sulphur dioxide (5, p. 236) over a range of temperatures. A large-scale deviation plot showed that the two sets were in agreement within the precision of the measurements, i.e., 0.01 atm. at the lower pressures to 0.02 atm. at the higher. The measured vapour pressures for Freon at 10°, 20°, and 30° C. agreed within the same limits with those reported by Gilkey, Gerard, and Bixler (3).

In Fig. 1, *C* is a glass bulb which serves as a gas reservoir (volume, determined by filling with water and weighing, 5.424 litres) and *D* is a mercury

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manometer that serves to determine the pressure in *C;* the mercury level in *D* was read on a plate glass scale similar to those used in this laboratory (see reference (4)). The dotted line in the figure indicates a second air thermostat held at 25.00 ± 0.05° C.; taps 1 and 2 are enclosed in a small copper box in this thermostat so that they can be manipulated without disturbing the temperature of bulb *C*.

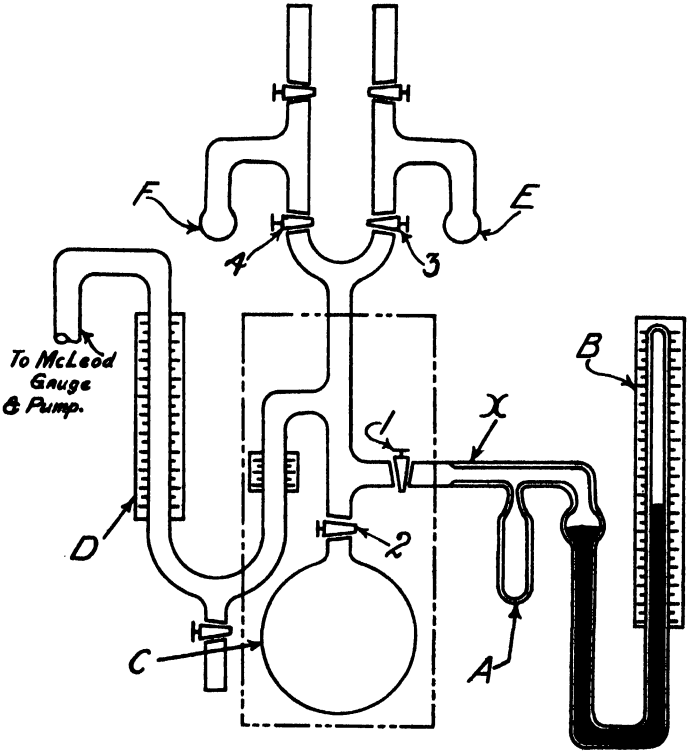

FIG. 1

Freon and carbon dioxide, after being dried by passage over Anhydrone, were condensed under vacuum with liquid air in the small side tubes *E* and *F;* the Freon was allowed to melt and boil to remove traces of dissolved air, and was then frozen again. The whole apparatus was evacuated, and the reading corresponding to vacuum on manometer *D* was taken. Tube *F* was then allowed to warm and carbon dioxide was allowed to pass into the apparatus with tap 1 closed until the pressure had attained the desired value; tap 4 was then closed and the carbon dioxide in *F* was again frozen with liquid air. After *C* had come to temperature equilibrium, the pressure was read on *D*, a suitable amount of carbon dioxide was condensed into *A* through tap 1 with liquid air, and the final pressure in the apparatus to the left of tap 1 was read. From the two pressure readings, the known volume of *C* and of the lines, and the equation of state, it was then possible to compute the number of moles of carbon dioxide frozen in *A*. The apparatus was next evacuated, and the procedure repeated with the Freon in tube *E*. With *A* still immersed in liquid air, the heavy glass capillary lead was next sealed off at *x*, and the water-bath filled and brought on temperature. To hasten attainment of equilibrium, the contents of *A* was stirred by a glass plunger with soft iron core, actuated by an electromagnet surrounding *A*. In all cases the final temperature was approached both from the side of higher and of lower values, and it was only when the two pressure readings agreed within the precision of the measurements that temperature equilibrium was assumed to be attained. To compute the composition of the system from the pressure readings, the equation of state of Beattie and Bridgeman was employed for carbon dioxide (1) and that of Buffington and Gilkey for Freon (2).

It should be noted that the composition obtained as described is that of the system as a whole and not that of the condensed phase; see reference (4). It is possible, however, by a short series of approximations to make a moderately accurate correction for this by assuming that the composition of the vapour in equilibrium with the condensed phase is given by Raoult's law, since the volume of the vapour above the liquid—approximately 3 cc.—is known from the dimensions of the apparatus and the volume of the liquid phase. With from 0.07 to 0.10 moles of Freon and from 0.005 to 0.075 moles carbon dioxide in the system, the correction varied from 0.3 mole % for the runs weakest in carbon dioxide to slightly over 1% for those richest in carbon dioxide. We believe that the corrected liquid compositions are probably accurate to 0.1 mole % or better.

Results

Table I gives for 10° and for 20° C. the observed vapour pressures in atmospheres as a function of the liquid mole fraction of the carbon dioxide; the deviation function δ, recorded in the third column of the table and plotted in Fig. 2, is defined by

TABLE I

10° C.			20° C.		
N_{CO_2}	P, atm.	δ, atm.	N_{CO_2}	P, atm.	δ, atm.
0	4.17	0	0	5.59	0
0.0466	6.25	+0.20	0.0460	7.98	+0.05
0.1041	8.94	+0.58	0.1037	11.19	+0.32
0.2078	13.25	+0.71	0.2068	16.24	+0.12
0.2496	14.70	+0.49	0.2474	17.87	−0.32
0.3277	17.26	−0.10	0.3252	20.79	−1.35
0.4079	20.04	−0.54	0.4063	24.43	−1.85
0.5403	24.98	−0.93	—	—	—

$$P = P_F^\circ + N_{CO_2}(P_{CO_2}^\circ - P_F^\circ) + \delta \tag{1}$$

where P_F° and $P_{CO_2}^\circ$ are the vapour pressures of Freon and carbon dioxide at the temperature in question; thus if the vapour were a perfect gaseous solution, the liquid obeyed Raoult's law, and the thermodynamic potentials of both components in the liquid were independent of pressure, δ would be identically zero. It is apparent from Fig. 2 that the deviations from Raoult's law cannot be serious, thus providing some justification for the method discussed above of computing the liquid composition from that of the system. It should be noted that the deviations are positive at the lower carbon dioxide concentrations and negative at the higher, and that for a given concentration the deviation becomes more negative with rising temperature.

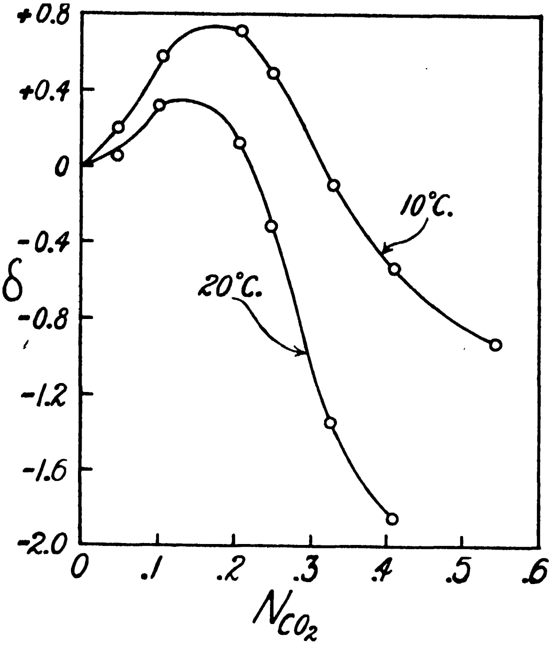

Fig. 2.

Table II gives the vapour pressure for round values of the liquid composition and also the temperature coefficient Δ log P/Δ $(1/T)$; these latter quantities may be used to obtain rough estimates of the vapour pressures at higher temperatures. An idea of how much reliance may be placed on such an

TABLE II

N_{CO_2}	$P_{10°}$	$P_{20°}$	$\Delta \log P/\Delta(1/T)$	N_{CO_2}	$P_{10°}$	$P_{20°}$	$\Delta \log P/\Delta(1/T)$
0	4.17	5.59	−1055	0.35	18.00	21.86	−700
0.05	6.44	8.24	890	0.40	19.74	24.15	725
0.10	8.74	10.99	825	0.45	21.59	—	—
0.15	10.91	13.55	780	0.50	23.45	—	—
0.20	12.94	15.92	745	0.55	25.35	—	—
0.25	14.74	17.94	710	1.00	44.41	56.50	−860
0.30	16.36	19.79	−685	—	—	—	—

extrapolation may be obtained from Table III, which gives the results of a few measurements carried out at 30° C. The first two lines give the liquid mole fraction of carbon dioxide and the observed vapour pressure at 30° C.; the third and fourth lines the corresponding vapour pressures at 10° C. (obtained from the plot of Fig. 2) and the temperature coefficients, and the last line the value at 30° C. computed from that for 10° C. and the temperature coefficient. It is apparent that for solutions low in carbon dioxide, the extrapolation gives reliable results, but that for solutions high in carbon dioxide it can give little more than an order of magnitude. On the other hand, since this method gives results that are too low, and the assumption that Raoult's law is obeyed gives results that are on the whole too high, the two used in conjunction should fix rough limits for the vapour pressures at higher temperatures.

TABLE III

N_{CO_2}	0	0.0454	0.2063	0.2462	0.3216
$P_{30°}$, obs.	7.34	10.08	19.79	21.62	25.06
$P_{10°}$	4.17	6.22	13.19	14.60	17.05
$\Delta \log P/\Delta(1/T)$	−1055	−900	−740	−710	−690
$P_{30°}$, calc.	7.35	10.08	19.62	21.38	24.68

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ACETYLATION AND BENZOYLATION OF DIBASIC SUGAR ACIDS[1]

BY M. ADELMAN[2] AND J. G. BRECKENRIDGE[3]

Abstract

Fully acetylated mucic acid, D-glucosaccharic anhydride, D-mannosaccharic anhydride, and α-D-glucopentahydroxypimelic acid have been prepared by the action of acetyl chloride on the neutral zinc salts of the corresponding acids. Fully benzoylated mucic, D-glucosaccharic, and D-mannosaccharic acids have been prepared in a similar manner. The action of acyl or aroyl halides on the neutral zinc salts of the dibasic sugar acids is proposed as a general method for preparation of the fully substituted derivatives.

The preparation of fully acylated or aroylated dibasic sugar acids has not been extensively investigated, and no generally applicable method for the preparation of such compounds has been reported. The only fully acetylated dibasic acids described to date are diacetyl-D-tartaric acid (1, 2, 3, 11) tetra-acetyl mucic acid (7, 9, 13), and tetra-acetyl allomucic acid (4). Dibenzoyl-D-tartaric acid (10) is the only fully benzoylated compound of this type recorded. No fully acetylated or benzoylated derivatives have been prepared from acids normally existing as lactones. A method has been developed recently for the preparation of fully acetylated aldonic acids by the acetylation of the aldonamide with acetic anhydride and zinc chloride (12), or by the acetylation of the cadmium aldonate with acetic anhydride and dry hydrogen chloride (8).

In the course of another investigation it was necessary to prepare fully acetylated α-D-glucopentahydroxypimelic acid, and a method was developed using acetyl chloride and the neutral zinc salt of the dibasic acid. The product was obtained in good yield, and it was thought that the method might be extended to the preparation of similar derivatives. In order to test the generality of the procedure, the acids chosen for experiment were (i) mucic acid, existing normally as the free acid, (ii) D-glucosaccharic acid, existing as the monolactone, and (iii) D-mannosaccharic acid, existing as the dilactone. The action of acetyl chloride on the neutral zinc salts of these acids resulted in the formation of the fully acetylated acid or acid anhydride, and the use of benzoyl chloride under similar conditions gave the fully benzoylated derivatives, with varying amounts of tribenzoylated derivatives as additional products. The results obtained would seem to indicate that a general method is available for the preparation of this type of compound.

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ont. Condensed from a portion of a thesis submitted in partial fulfilment of requirements for the degree Ph.D.

[2] *Graduate student.*

[3] *Associate Professor of Chemical Engineering.*

Experimental

Zinc mucate.—A filtered solution of zinc acetate dihydrate (28 gm., 0.128 mole) in 250 ml. water was added to a boiling solution of mucic acid (25 gm., 0.119 mole) in 1500 ml. water. The resulting white crystalline precipitate (together with a second crop obtained by concentrating the mother liquor) weighed 35.4 gm. (91%). Found: ZnO, 24.7%. Calc. for $C_6H_8O_8Zn \cdot 3H_2O$: ZnO, 24.9%.

Zinc D-glucosaccharate.—A filtered solution of zinc acetate dihydrate (11.5 gm., 0.052 mole) was added to a solution of 10 gm. (0.05 mole) of D-glucosaccharolactone (m.p. 103° to 108° C.) in 1 litre water. The mixture was digested on the steam-bath for three hours, and the white crystalline product formed (together with a second crop) weighed 14.1 gm. (99%). Found: ZnO, 26.9%. Calc. for $C_6H_8O_8Zn \cdot 1.5\ H_2O$: ZnO, 27.1%.

Zinc D-mannosaccharate.—This was prepared from D-mannosaccharodilactone, obtained from D-mannitol by the method of Easterfield (5), and from D-mannose by the method of Haworth, Heslop, Salt, and Smith (6). A filtered solution of 7.9 gm. (0.036 mole) zinc acetate dihydrate in 250 ml. water was added to 5.0 gm. (0.035 mole) of the dilactone dissolved in 250 ml. water. The solution was concentrated *in vacuo* at 35° to 40° C. to 250 ml., made up to 400 ml. with distilled water, and allowed to stand at room temperature. Crystals began to deposit within 24 hr., and after standing for a week, 6.0 gm. (80%) of the crystalline zinc salt was obtained. Found: ZnO, 25.1%. Calc. for $C_6H_8O_8Zn \cdot 3H_2O$: ZnO, 24.9%.

Zinc α-D-glucopentahydroxypimelate.—Calcium α-D-glucopentahydroxypimelate (25 gm., 0.09 mole) was suspended in 250 ml. water, and 12 ml. concentrated nitric acid (0.095 equiv.) was added with stirring until the suspended salt had all dissolved. Zinc carbonate (15 gm., 0.12 mole) was then added to the solution, the mixture heated to gentle boiling, and digested for an hour. The mixture was then filtered hot, the filtrate decolorized with Norit, concentrated to 100 ml. *in vacuo*, and an equal volume of ethanol added. The precipitate was washed with 80% ethanol, and weighed 23.2 gm. (85%). Found: ZnO, 26.3%. Calc. for $C_7H_{10}O_9Zn$: ZnO, 26.8%. The salt precipitates as the hydrate (1.5 H_2O), but was dehydrated before analysis.

Tetra-acetyl mucic acid.—A suspension of 1.2 gm. oven-dried zinc mucate in 5 ml. acetyl chloride was refluxed at 60° C. for 1.5 hr. The acetyl chloride remaining was distilled off *in vacuo* and ice–water added to the residue. A pale yellow crystalline solid was obtained, which after drying at 105° C. for several hours weighed 1.2 gm. (93%), and had a melting point of 238° C.* One recrystallization from 95% ethanol raised the melting point to 243° C. (Recorded in literature, m.p. 243° C.)

Tetra-acetyl D-glucosaccharic anhydride.—Zinc D-glucosaccharate hemihydrate (2.4 gm., 0.0085 mole) was weighed into a flask. Acetyl chloride (5 ml., 0.07 mole) was added through a reflux condenser, and, after the reaction subsided, the mixture was refluxed at 60° C. for an hour. The excess acetyl chloride was removed *in vacuo*, and the remaining viscous oil treated with 25 ml. chloroform. The chloroform solution, after being washed with dilute hydrochloric acid and water, and dried over sodium sulphate, was concentrated to half volume, and on the addition of petroleum ether a white crystalline product was obtained in about 35% yield. A recrystallization from ethyl-acetate–petroleum-ether gave a product with a melting point of 178° to 178.5° C., $[\alpha]_D^{22}$ + 149.7° (c = 0.77 in dry acetone). Found*: C, 46.57, 46.51; H, 4.45, 4.32%. Calc. for $C_{14}H_{16}O_{11}$: C, 46.57; H, 4.48%.

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* *Melting points are corrected.*

Tetra-acetyl D-mannosaccharic anhydride.—Prepared in the same manner as the previous compound, yield 37.5%, m.p. 177° to 178° C., $[\alpha]_D^{22}$ + 244° (c = 1.07 in dry acetone). Found: C, 46.40, 46.67; H, 4.37, 4.39%. Calc. for $C_{14}H_{16}O_{11}$: C, 46.57; H, 4.48%.

α-D-glucopenta-acetoxypimelic acid.—Prepared in a similar manner. The washed and dried chloroform extract on concentrating to dryness *in vacuo* yielded a sandy-coloured resin. This could not be crystallized, but on standing in contact with water for several days a 70% yield of white crystals was obtained. After recrystallization from ethyl-acetate–petroleum-ether the melting point was 122° C. Found: C, 44.98, 45.02; H, 5.03, 5.07%. Calc. for $C_{17}H_{22}O_{14}$: C, 45.33; H, 4.92%.

Tetrabenzoyl mucic acid.—Oven-dried zinc mucate (5.0 gm., 0.017 mole) was mixed with 12 ml. (0.104 mole) of benzoyl chloride in a flask, and heated under a reflux condenser on the water-bath. A reaction began at 45° C. and hydrogen chloride was evolved. The mixture was maintained at 45° C. until reaction had ceased and the material in the flask was solid. This was then broken up, and washed with dilute hydrochloric acid and water. The product was crystallized from 100 ml. 95% ethanol, and a second crop obtained on concentration of the mother liquor. The combined crops were washed several times with cold benzene and dried. Yield, 4.1 gm. (39%), m.p. 198° to 198.5° C. Recrystallization from benzene did not alter the melting point. Found: C, 65.50, 65.57; H, 4.30, 4.28%. Calc. for $C_{34}H_{26}O_{12}$: C, 65.17; H, 4.18%.

Tetrabenzoyl D-glucosaccharic acid.—Zinc D-glucosaccharate hemihydrate (1.0 gm., 0.004 mole) was mixed with 2.4 ml. (0.022 mole) of benzoyl chloride and warmed on a water-bath under a reflux condenser. The reaction began at 80° C., and the mixture was held at that temperature for an hour. The product was isolated and purified as for the mucic acid derivative. Yield, 0.8 gm. (36%). After several recrystallizations from ethyl-acetate–petroleum-ether the compound had a melting point of 173° C., $[\alpha]_D^{22}$ + 102.7° (c = 0.80 in dry acetone). Found: C, 65.16, 65.18; H, 4.28, 4.26%. Calc. for $C_{34}H_{26}O_{12}$: C, 65.17, H, 4.18%.

Tetrabenzoyl D-mannosaccharic acid.—Reaction was carried out in the same manner as the previous experiment. Only a portion of the reaction product would dissolve in hot 95% ethanol, and the ethanol-insoluble material was thoroughly washed with hot ethanol and recrystallized several times from ethyl-acetate–petroleum-ether. Yield 24%, m.p. 186° to 187° C., $[\alpha]_D^{22}$ + 267° (c = 0.55 in dry acetone). Found: C, 64.74, 65.31; H, 4.20, 4.24%. Calc. for $C_{34}H_{26}O_{12}$: C, 65.17; H. 4.18%.

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* *Carbon–hydrogen microanalyses by A. E. Ledingham and Mrs. E. Mason.*

Tribenzoyl D-mannosaccharolactone.—The ethanol solution from the previous experiment was decolorized with Norit and concentrated to 15 ml. The fine, needle-like crystals were washed with 90% ethanol and dried at 90° C. Yield, 1.1 gm. (66%). After recrystallization from ethyl-acetate–petroleum-ether the melting point was 196° C., and $[\alpha]_D^{22}$ + 245° (c = 1.07 in dry acetone). No mutarotation was observed after 96 hr. Found: C, 64.27, 64.60; H, 3.97, 4.00%. Calc. for $C_{27}H_{20}O_{10}$: C, 64.23; H, 3.97%.

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STUDY ON THE SYNTHESIS OF VALINE BY THE STRECKER METHOD[1]

By Roger Gaudry[2]

Abstract

A systematic investigation of the synthesis of *dl*-valine by the Strecker method, starting from isobutyraldehyde, has been made. The potassium-cyanide–ammonium-chloride procedure, as modified by us, has been found to be the most convenient for the large scale laboratory preparation of this amino acid, considering the over-all yield, the purity of the amino acid, and the time required, as well as the ease of preparation. A continuous ether extraction of the amino nitrile has been introduced. This accounts for the high yield and easy separation of the pure amino acid.

Introduction

The principle of the Strecker method (8) for the synthesis of amino acids has been known for nearly a century. Although it has been applied by many investigators to the synthesis of about 10 naturally occurring amino acids, the method, despite various improvements, does not seem to be widely used for the large scale preparation of amino acids, except perhaps for alanine, glycine, and possibly serine.

Now that many aldehydes are commercially available, it seems worth while to investigate further the method and the various improvements that have been suggested, and to try to ascertain whether the method can be modified so as to give better yields than those usually reported.

The most careful studies made of the Strecker method are those of Cocker and Lapworth (3) and Bucherer and collaborators (1, 2). Important also are the syntheses by the Strecker method published in *Organic Syntheses* (7). But it is indeed remarkable that these authors have worked mainly with ketones as starting material, and rarely with aldehydes, which might have led to naturally occurring amino acids.

The study of the synthesis of valine was considered desirable because of the high cost of the commercial synthetic product, the low cost of isobutyraldehyde as starting material, and the fact that there is no known practicable procedure for the isolation of the natural form of valine from protein hydrolysates.

Valine was synthesized from isobutyraldehyde by Lipp in 1880 (4), from hydrocyanic acid and ammonia, but the yield is not reported. No further

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work on the subject appears to have been published. The synthesis of valine from isobutyraldehyde has been investigated by us as follows:

(1) Using alkali cyanides and ammonium chloride.
(2) Using free hydrocyanic acid and ammonia.
(3) Via the bisulphite addition compound.
(4) Via the corresponding hydantoin.

Part I

THE SYNTHESIS OF *dl*-VALINE FROM POTASSIUM CYANIDE AND AMMONIUM CHLORIDE

Cocker and Lapworth have recommended (3) the exclusion of even small amounts of alkali metals in the synthesis of the more soluble amino acids by the Strecker method. We have found on the contrary that *dl*-valine, which is a very soluble amino acid, can be satisfactorily synthesized from potassium cyanide and ammonium chloride, provided the amino nitrile is extracted from the aqueous solution before being hydrolysed. A continuous ether extractor is very convenient, since it allows for the complete extraction, with a comparatively small volume of ether, of an amino nitrile which is not contaminated by alkali metals.

After the synthesis had been carried out under various experimental conditions, it was found that:

1. Only freshly distilled isobutyraldehyde should be used. The commercial aldehyde employed as received gave much lower yields.
2. The reaction between the aldehyde and the cyanide and ammonium salt is best carried out at room temperature. Some cooling is recommended while the aldehyde is added to the mixture of cyanide and ammonium salt, to avoid overheating, but no further cooling is necessary.
3. An excess of potassium cyanide and ammonium chloride does not increase the yield. But the presence of an excess of ammonia in the reaction mixture significantly increases the yield. The presence of a little ether is also beneficial.
4. If the amino nitrile is extracted by shaking with several successive portions of ether, instead of using a continuous ether extractor, the overall yield of crude valine is about 10% lower.
5. Hydrolysis of the amino nitrile with hydrochloric acid is to be recommended. This acid gives as good a yield as sulphuric acid. It enables easier separation of the amino acid from the reaction mixture, and also avoids the precipitation, as barium sulphate, of the large excess of sulphuric acid necessary for the hydrolysis.
6. The amino acid can be isolated by the glacial acetic acid method described by Marvel (6), but the isolation is more easily and rapidly effected by dissolving the *dl*-valine hydrochloride in absolute ethyl alcohol,

filtering the insoluble salts, and precipitating the valine with a slight excess of pyridine.

By following in detail the experimental conditions described below, a 65% over-all yield of nearly pure valine, or a 62.5% yield of very pure valine, is obtained.

EXPERIMENTAL

dl-Valine

A mixture of ammonium chloride (60 gm., 1.1 mole), potassium cyanide (66 gm., 1.0 mole), water (400 ml.), and concentrated ammonium hydroxide (155 ml.) is placed in a one litre, three-necked flask half immersed in cold running water and fitted with a separatory funnel, mechanical stirrer, and a long stem thermometer dipping into the liquid. The mixture is stirred and freshly distilled isobutyraldehyde (91 ml., 1.0 mole) is added drop by drop. The addition of the aldehyde requires about half an hour, in the course of which the temperature of the reaction mixture reaches about 40° C., but rapidly decreases to room temperature when the addition of the aldehyde is complete. Ethyl ether (100 ml.) is then added, and the mixture is continuously stirred for about six hours. After it has stood overnight, the reaction mixture is poured into a continuous ether extractor and extracted with ether (250 ml.) for 48 hr. The ether is then evaporated *in vacuo* at room temperature, and the residual pale yellow liquid is treated with concentrated hydrochloric acid (500 ml.). The mixture is shaken, allowed to stand at room temperature overnight, and boiled under reflux for 24 hr. It is then evaporated to dryness *in vacuo* on the water-bath, water (300 ml.) is added, and the solution is boiled under reflux with charcoal for half an hour, filtered, and again evaporated to dryness *in vacuo*. The solid residue is taken up with absolute ethyl alcohol (500 ml.) and boiled under reflux for a few minutes, and the solution is cooled, filtered from insoluble ammonium chloride, and pyridine (100 ml.) is added. The solution is well shaken and allowed to stand overnight in the ice-box. The precipitated *dl*-valine is filtered on a Büchner funnel, washed with successive (25 ml.) portions of absolute ethyl alcohol until free from pyridine, and allowed to dry. The yield of perfectly white, nearly pure valine is 76.3 gm., 65%. The amino acid is dissolved in boiling water (490 ml.), and 95% alcohol (500 ml.) is added, and the mixture is left overnight in the ice-box. The amino acid is filtered, washed with 95% alcohol, and dried. Yield, 63.2 gm. The filtrate is evaporated, the residue is dissolved in boiling water (55 ml.), and 95% alcohol (60 ml.) added; on cooling, a second crop of 8.7 gm. separates. A third crop of 1.3 gm. may be obtained by working up the residues. Total yield, 73.2 gm., 62.5%. The recovery in the crystallization is 96%. The very pure amino acid obtained in this way contains the theoretical amount of nitrogen. Found (Kjeldahl): N, 12.00%. Calc. for $C_5H_{11}O_2N$: N, 11.96%. It melts in a sealed tube at 289° to 290° C.*

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* *Melting points are not corrected.*

Part II

THE SYNTHESIS OF *dl*-VALINE FROM HYDROCYANIC ACID AND AMMONIA

In their study of the Strecker method for the synthesis of amino acids, Cocker and Lapworth (3), who used an excess of hydrocyanic acid and ammonia, claimed an average yield of about 70% of amino acids, but they did not prepare *dl*-valine, although they made *dl*-norvaline in a 68% yield.

We have prepared *dl*-valine from isobutyraldehyde, using an aqueous solution of hydrocyanic acid and concentrated ammonia. Our results indicate that an excess of ammonia is essential to obtain a good yield of amino acid, but that an excess of hydrocyanic acid does not increase the yield. Using two moles of hydrocyanic acid and two moles of ammonia per mole of aldehyde, a [illegible]0% yield of *dl*-valine is obtained. With two moles of hydrocyanic acid and four moles of ammonia, the yield is 44.5%. But with one mole of hydrocyanic acid and four moles of ammonia, a 58.5% yield of *dl*-valine is obtained.

It is remarkable that the best yield obtained with free hydrocyanic acid is from 10 to 12% lower than the yield claimed for similar compounds by Cocker and Lapworth, and about 7% lower than the best yield obtained in the synthesis of *dl*-valine from potassium cyanide, ammonium chloride, and ammonia.

EXPERIMENTAL

dl-Valine

Isobutyraldehyde (91 ml., 1 mole) is added dropwise to a cooled mechanically stirred solution containing hydrocyanic acid (27 gm., 1 mole), concentrated ammonia (270 ml., 4 moles), and water (100 ml.). After 12 hr. of stirring at room temperature, the mixture is extracted with ether for 24 hr. in a continuous ether extractor, the ether is evaporated *in vacuo*, and the residue is hydrolysed by boiling under reflux for 24 hr. with concentrated hydrochloric acid (500 ml.). The valine is isolated as described in Part I. Yield, 68.4 gm., 58.5%.

Part III

THE SYNTHESIS OF *dl*-VALINE VIA THE BISULPHITE ADDITION COMPOUND

We have investigated the preparation of *dl*-valine by the reaction of isobutyraldehyde with sodium acid sulphite and potassium cyanide. The main reason for this was to ascertain whether, by using an excess of sodium acid sulphite and potassium cyanide, the yield of cyanhydrin and that of *dl*-valine could be increased.

Using 1.5 moles of sodium acid sulphite and 1.5 moles of potassium cyanide per mole of aldehyde, a 46% yield of *dl*-valine is obtained, while, using one mole of acid sulphite and one mole of cyanide per mole of aldehyde, the yield is increased to 53.5%.

EXPERIMENTAL

dl-Valine

Isobutyraldehyde (91 ml., 1 mole) is added dropwise to a cooled and mechanically stirred solution of sodium acid sulphite (105 gm., 1 mole) in water (100 ml.). A solution of potassium cyanide (66 gm., 1 mole) in water (100 ml.) is then added slowly to the cooled and stirred paste of bisulphite addition compound, and stirring is continued for one hour at room temperature. The mixture is extracted with ether for 24 hr. in a continuous ether extractor, the ether is evaporated *in vacuo*, and the resulting free cyanhydrin is added dropwise to mechanically stirred, concentrated ammonia (270 ml., 4 moles). After six hours of stirring at room temperature, the mixture is extracted with ether for 24 hr. in a continuous ether extractor, the ether is evaporated *in vacuo*, and the resulting amino nitrile is hydrolysed by boiling under reflux for 24 hr. with concentrated hydrochloric acid (500 ml.). The valine is isolated as described in Part I. Yield, 62.5 gm., 53.5%.

Part IV

THE SYNTHESIS OF *dl*-VALINE VIA THE 5-ISOPROPYLHYDANTOIN

Bucherer and collaborators (1) have claimed that they could obtain very high yields of hydantoins, usually from 80 to 90%, by allowing an aldehyde or a ketone bisulphite compound to react with a large excess of potassium cyanide and ammonium carbonate in 50% alcohol. We have not been able to obtain similar results with isobutyraldehyde. The reason probably is that 5-isopropylhydantoin is difficult to separate from the large amount of potassium carbonate formed as a by-product of the reaction. And it must be kept in mind that Bucherer worked only with ketones, or with aldehydes containing an aromatic nucleus, therefore his hydantoins were much less soluble in water than 5-isopropylhydantoin.

We have prepared the hydantoin by using a method that does not require the separation of the hydantoin from alkali salts. It consists in preparing the free cyanhydrin in the manner described in Part III, and allowing it to react with an excess of ammonium carbonate. Pure 5-isopropylhydantoin is obtained in a 77% yield.

This preparation of 5-isopropylhydantoin is interesting in so far as the hydantoin can be hydrolysed to *dl*-valine with a very high yield, for an 85% yield for the hydrolysis would mean an over-all yield of 65%, which we had already achieved by the method described in Part I.

The acid hydrolysis of hydantoins usually gives poor yields because the hydantoin ring is more readily closed than opened in the presence of acids. However, a 63% yield of valine was obtained by boiling under reflux 5-isopropylhydantoin for 60 hr. with 20% hydrochloric acid. But the hydantoin is readily hydrolysed in an 85% yield by refluxing at atmospheric pressure with barium hydroxide, although we have not been able to achieve anything like the 95% yield claimed by Livak *et al.* (5) by hydrolysis, under pressure, of 5-(β-methylmercaptoethyl)hydantoin with barium hydroxide.

EXPERIMENTAL

5-Isopropylhydantoin

The cyanhydrin is first prepared in the manner described in Part III, starting with one mole (91 ml.) of isobutyraldehyde. After it has been extracted from the reaction mixture the cyanhydrin is added to a solution of ammonium carbonate (230 gm., 2.4 moles) in water (400 ml.), and the mixture is kept at 50° C. for five hours. After being heated at 95° to 100° C. for one hour to remove the excess of ammonium carbonate, the solution is filtered hot and concentrated to a small volume. On cooling, 5-isopropylhydantoin separates in long needles. Crude yield of yellow-coloured hydantoin: 119 gm., 84%. After two crystallizations from hot water, including treatment with Norite, the yield is: 109 gm., 77%; m.p. 142° to 143° C. After many recrystallizations: m.p. 144° to 145° C. Found (Kjeldahl): N, 19.4%. Calc. for $C_6H_{10}O_2N_2$: N, 19.7%.

dl-Valine

In a 500 ml. round bottomed flask are placed 5-isopropylhydantoin (14.2 gm., 0.1 mole), barium hydroxide (80 gm. of the octahydrate, 0.25 mole), water (100 ml.) and the mixture is boiled under reflux for 24 hr., the top of the condenser being fitted with a soda-lime tube. Carbon dioxide is then passed into the mixture until no more precipitate forms. The solution is filtered hot, the precipitate is washed with hot water, and the filtrate is evaporated to dryness *in vacuo*. The residue is *dl*-valine, which is recrystallized in the usual way. Yield, 9.8, gm., 85%.

Conclusion

These results seem to indicate that the reaction of cyanhydrin formation is not an equilibrium reaction, since an excess of nitrile is not beneficial, while the reaction between the aldehyde or the cyanhydrin with ammonia is definitely an equilibrium reaction, for an excess of ammonia gives a much better yield. Furthermore, the best method for the large scale laboratory preparation of *dl*-valine is probably the Strecker method as modified by us, using potassium cyanide, ammonium chloride, ammonia, and a continuous ether extractor for the isolation of the amino nitrile. Following a typical run starting with five moles (360 gm.) of isobutyraldehyde, more than 350 gm. of very pure, recrystallized valine was obtained. About the same over-all yield is obtained if the synthesis is made by way of the hydantoin, followed by hydrolysis with barium hydroxide, but this procedure requires more time and manipulation, and the required number of recrystallizations of the product is one more than that necessary when the first procedure is used.

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